

Interfacial Phenomena in Countercurrent Processes using Supercritical Fluids

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INTRODUCTION

Performance and efficiency of industrial processes are generally influenced by interfacial effects. In any process involving more than one homogeneous phase, interfaces either determine the procedure itself like in liquid - liquid extraction or the final product like margarines or coatings. High pressure processes are affected in the same way, only that interfacial phenomena are not so easily accessible. Certain effects are often assumed to occur just by deduction from the final result. Methods have been developed recently in order to quantify dominating interfacial properties at high pressures. The interfacial tension plays an important role among these since this measure resembles the energy for creating new interface. While the interfacial tension is used to describe fluid interfaces the analogous measure for solid - fluid interfaces is directly named interfacial energy. The interfacial energy on its turn is related to the wetting behavior of liquids on solid surfaces. It becomes quite clear that any liquid - fluid mass transfer operation is strongly influenced by the interfaces being present within the process. Since the rate of transferred moles is directly related to the extension of the interface by

$$\dot{N} = kA \cdot \Delta c \quad (1)$$

the variety and complexity of the associated interfacial phenomena becomes apparent.

Table 1 gives an overview on different types of interfacial phenomena as they affect high pressure processes that involve supercritical fluids.

Phenomena	Process	Interfacial Property to measure
Drop formation	Spraying (RESS, GAS, etc.)	IFT, drop size, drop velocity
Bubbles	Bubble column	IFT, bubble size/shape
Wetting	Packed column	Contact angle, wetting
Foam	Bubble column	Foam stability, IFT
Nucleation	Polymer processing	Crit. Pressure difference, IFT
Emulsion	Reverse micelles	Phase behavior
Interfacial convection	Mass transfer operations	Schlieren - method
Coalescence	Mixer-Settler	Coalescence rate

Table 1: Interfacial phenomena in supercritical fluid processing

MEASUREMENT OF THE INTERFACIAL TENSION

Since the thirties of the past century the pendant drop method is known for determining interfacial tension from drop shapes that are generated inside a view chamber at elevated pressure.

During decades experimental values were subject to fairly high errors due to analogous photographing images and an empirical evaluation method [1]. Electronic data processing allowed later to digitalize drop images and solve the theoretical equation of a drop profile exactly according to physical laws [2]. The measuring principle is based on the pressure resulting from curvature of fluid interfaces which is described by the Laplace law:

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

As a consequence of this relation a liquid flows spontaneously into a capillary in case of wetting of the inner surface which is also called capillary action. Applied to a pendant drop the hydrostatic pressure needs to be accounted for in order to obtain an equation that describes the Laplace pressure at any height of the drop:

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\sigma}{R_0} - \Delta \rho g z \quad (3)$$

or as a differential equation:

$$\sigma \left(\frac{d\phi}{ds} + \frac{\sin \phi}{x} \right) = \frac{2\sigma}{R_0} - \Delta \rho g z \quad (4)$$

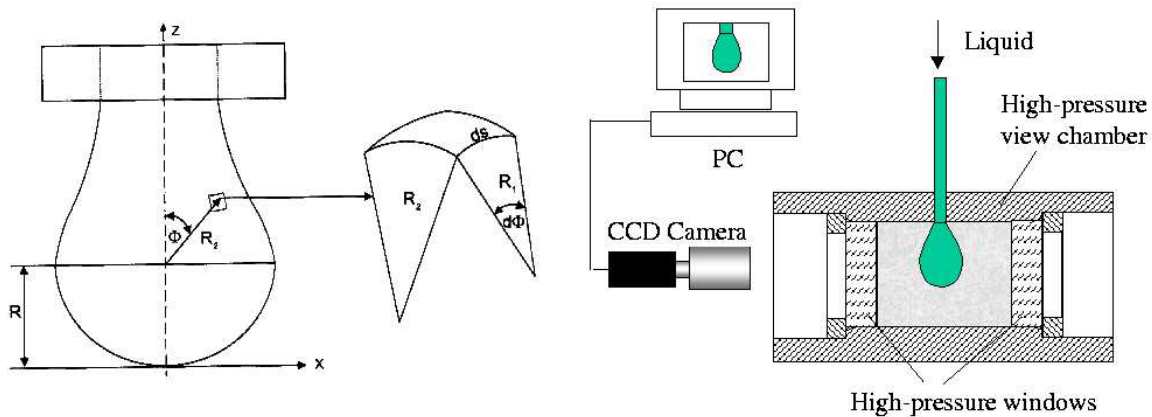


Figure 1: Coordinates of a pendant drop

For adaptation of the pendant drop measuring principle to high pressure, drops are generated within a high pressure view chamber like shown in fig. 1. After recording by means of a CCD-camera connected to a personnel computer, drop shapes are evaluated for determination of the interfacial tension with help of the DSA (drop shape analysis) programme from company KRÜSS, Hamburg. Fig 2 shows some examples of conducted measurements. All experiments showed decreasing interfacial tension at higher pressures due to the solvation of CO₂ in the liquid phase. The experiments also showed the influence of surface active compounds. A small amount of the surfactant Triton X in water leads to a strong decrease of the interfacial tension compared to pure water. At first sight it is surprising that the interfacial tension of the system water - Triton X - CO₂ increases at higher pressures. This behavior is based on the interaction between the three compounds. More Triton X is soluble in CO₂ at higher pressure. Less surfactant in the liquid phase leads to an increasing interfacial tension.

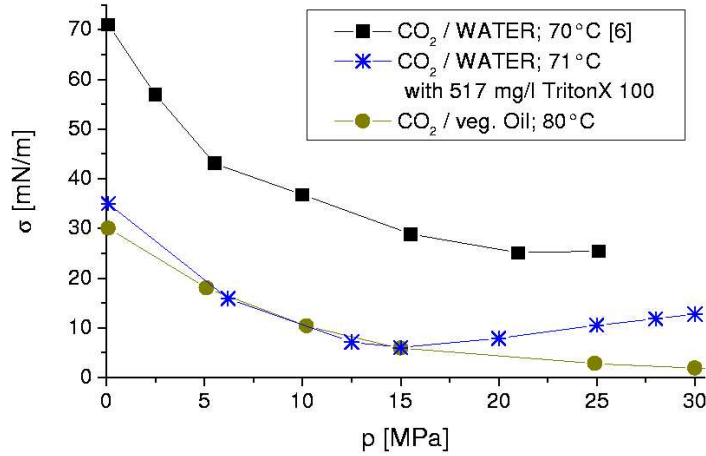


Figure 2: Some results of the measurement of interfacial tensions

Further materials for investigation include high viscous resins, silicone oils, crude oils, hydrocarbons, polymer-melt, liquid metals or lubricants. The surrounding phase can either be a gas like CO₂ or nitrogen or transparent liquids.

WETTING OF SOLID SUBSTRATES

Liquid-fluid extraction processes are often carried out in packed columns using either structured or unstructured packings. The task of the packings is to increase the liquid surface area by introduction of additional solid elements into the flow of the liquid phase. According to the wetting behavior, the liquid either spreads on the solid surfaces or gathers together forming single drops. The knowledge of the wetting behavior is important to scale the extraction process. A poor wetting behavior

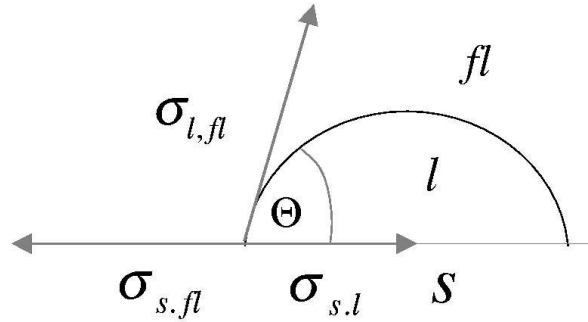


Figure 3: Contact angle and interfacial tension/energies acting at the three phase contact.

The wetting behavior is described by the so-called contact angle that on its turn depends not only on the drop liquid and the solid material, but also on the ambient liquid or gas and the structure of the solid surface. From thermodynamics a relationship between drop and ambient liquid, the contact angle and the interfacial energies of the solid surface in contact with the respective liquids may be deduced, called the Young's equation:

$$\sigma_{solid,fl} = \sigma_{liq,fl} \cos(\theta) + \sigma_{solid,liq} \quad (5)$$

The measurements of the contact angle can be conducted in a high-pressure view cell. A small droplet is produced on the surface (sessile drop) and recorded by a CCD-camera connected to a computer. The contour of the droplet can be evaluated for determination of the

contact angle with help of a computer program (DSA, KRÜSS). Two different kinds of measuring techniques have been developed: The first technique is a static measurement. The droplet is produced on the surface and evaluated. The second technique is the advancing contact angle. The size of the droplet is increased with time simultaneously measuring the contact angle. The limiting value of θ is taken to be the contact angle [3]. Fig. 4 shows some examples of conducted measu

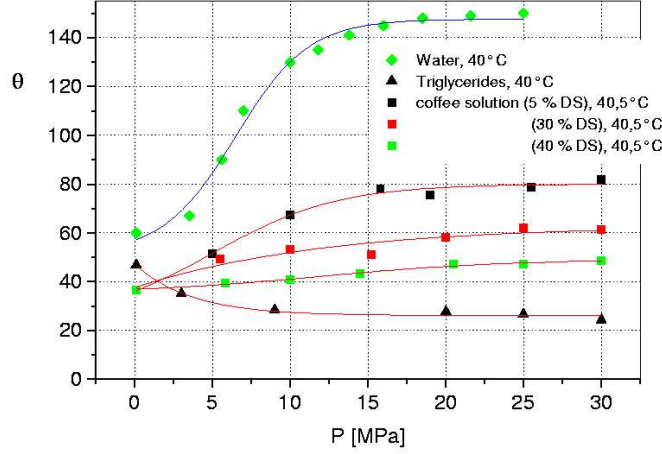


Figure 4: Contact angle of different liquids on stainless steel in CO₂-atmosphere

The relationship 5 may also be interpreted as a balance of forces in horizontal direction between the interfacial tension $\sigma_{liq,fl}$, the solid-(drop) liquid interfacial energy $\sigma_{solid,liq}$ and the solid-(surrounding) fluid interfacial energy $\sigma_{solid,fl}$. Analogous to liquid surface tension solid surfaces contain a surface energy which is decisive for whether a surface is rather oil or water wet, i.e. whether surface energy is low or high. Though, by changing properties of the liquid phase, wettability may considerably be enhanced.

To calculate the solid-fluid tension using equation 5 some assumptions have to be made: The free energy of adhesion between two phases may be written by the geometric mean of the free energies of cohesion of the separate phases [4]:

$$|\Delta F_{12}^a| = \sqrt{\Delta F_1^c \Delta F_2^c} = 2\sqrt{\sigma_1 \sigma_2} \quad (6)$$

Here

$$-\Delta F_{12}^a = \sigma_1 + \sigma_2 - \sigma_{12} \quad (7)$$

$$-\Delta F_1^c = 2\sigma_1, \quad -\Delta F_2^c = 2\sigma_2 \quad (8)$$

σ_1 and σ_2 are the surface free energies of the two separate pure phases. Equation 6 can also be transferred to:

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1 \sigma_2} \quad (9)$$

This equation shows a good approximation for fluorocarbon-hydrocarbon systems, but not for many water- organic liquid systems. To overcome this problem

$$\Phi = \frac{-\Delta F_{12}^a}{\sqrt{\Delta F_{12}^c \Delta F_{12}^c}} = \frac{\sigma_1 + \sigma_2 - \sigma_{12}}{2\sqrt{\sigma_1 \sigma_2}} \quad (10)$$

was introduced as a unique property of a pair of substances 1 and 2. Equation 9 can be written as:

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\phi\sqrt{\sigma_1\sigma_2} \quad (11)$$

Using a solid-liquid system in a surrounding fluid this equation becomes:

$$\sigma_{s,l} = \sigma_{s,fl} + \sigma_{l,fl} - 2\phi\sqrt{\sigma_{s,fl}\sigma_{l,fl}} \quad (12)$$

This equation can be combined with equation (5):

$$\sigma_{s,fl} = (1 + \cos\theta)^2 \sigma_{l,fl} / 4\phi^2 \quad (13)$$

It can be seen, that it is possible to calculate $\sigma_{s,fl}$ with the knowledge of the interfacial tension $\sigma_{l,fl}$ and the contact angle θ . This method was developed by Good & Girifalco [5].

Other theories for the calculation of the surface energies were introduced by Zisman [6], Fowkes [7] and Owens et. al. [8]. The known theories are usually applied to atmospheric conditions neglecting the influence of the (atmospheric) gas. Up to now, little is known about solid surface energies at elevated pressures and temperatures, when the surrounding phase might be any compressed gas or even supercritical fluid. In this case, the respective energy is called solid - fluid interfacial energy. It is no longer a material constant of the solid itself, but depends on the density and composition of the contacting phases.

As a first attempt to estimate solid-fluid interfacial energies the well defined system Teflon - N_2 has been examined. Table 2 shows the interfacial energy of Teflon in nitrogen atmosphere at increasing pressure deduced from the interfacial tension of toluene - nitrogen and the contact angle following an approach presented by Good & Girifalco [5] using an interaction parameter of $\phi = 0.98$ [9].

p [MPa]	$\sigma_{toluene,N_2}$ [mN/m]	θ	σ_{teflon,N_2} [mN/m]
0.1	57.5	93.0	22.6
9.0	51.3	102.0	13.9
18.0	46.1	110.5	9.7
20.0	44.5	112.5	9.3

Table 2: Experimental interfacial tension - energy and contact angle: teflon-toluene-nitrogen

Applicability of the used theory for determining interfacial energy of solids at elevated pressures can be tested by means of Young's law which is physically proven. Applying Young's equation (5), the toluene - teflon interfacial energy at atmospheric conditions may be determined from tab. 2:

$$\sigma_{teflon,toluene}(1bar) = \sigma_{teflon,N_2}(1bar) - \sigma_{toluene,N_2}(1bar) \cos\theta(1bar) = 25.6mN/m \quad (14)$$

Assuming this interfacial energy to be pressure invariant because of negligible amounts of nitrogen in the toluene phase, the contact angle at any pressure should be predictable:

$$\cos\theta(p) = \frac{\sigma_{teflon,N_2}(p) - \sigma_{teflon,toluene}}{\sigma_{toluene,N_2}(p)} \quad (15)$$

Recalculated values of the contact angle based on Young's law and using the interfacial energy of the solid from theories of Good & Girifalco coincide extremely well with experimental data (within 1% accuracy). The results prove that certain assumptions are allowed also

at high pressure which makes known theoretical approaches applicable. It has to be checked in future work, if the theories also lead to reasonable approximations in case solid surfaces of column packings. A further problem will be contacting phases strongly interacting with CO₂ at conditions of mutual solubilities.

CONCLUSIONS

Interfacial phenomena affect supercritical processing to a high extent by determining the required energy input for creating mass transfer area, formation of colloids and taking influence on the residence time via drop falling or bubble rising velocity. This paper shows methods for quantifying interfacial phenomena at elevated pressure in view of their interpretation with respect to the process. Decreasing interfacial tension at elevated pressure favors creation of new interface enhancing the efficiency of the liquid - supercritical process. In case solid packing is used, contact angle determines whether a falling film covers the solid surface or drops are just hindered from freely falling. Quite some experimental work still needs to be performed on process analysis as well as fundamental interfacial properties in order to gain reliable data sets for relating process behavior to interfacial phenomena in a quantitative way. Nevertheless, this work contributes to principle understanding of some dominating mechanisms in supercritical fluid processing that opens the way for taking influence on the process.

Symbols

A	area	$[m^2]$	c	concentration	$[mol/l]$
F_i	free energy	$[mN/m]$	k	mass transfer coefficient	$[m/s]$
\dot{N}	molar flow	$[mol/s]$	p	pressure	$[MPa]$
R_1, R_2	radii of curvature	$[m]$	ρ	density	$[kg/m^3]$
ϕ	interaction parameter	$[-]$	θ	contact angle	$[-]$
σ	interfacial tension	$[mN/m]$			

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