Application Report

Interfacial tension under non-standard pressure conditions

Application report:	AR235e
Industry section:	Petroleum, chemical, food technology
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Date:	2003
Method:	
Keywords:	High pressure, interfacial tension, surface tension, wetting, vacuum, extraction, fractionation

Drop Shape Analysis System DSA10

Interfacial tension and wetting in liquid-liquid separation technology

Introduction

Besides density and viscosity the knowledge of interfacial tension is of importance for the design of liquid-liquid separation equipment. For almost immiscible systems, e.g., consisting of water and a saturated hydrocarbon without functional groups the interfacial tension can be estimated by calculating the mean value of the surface tension of the single phases.
However, in the case of hydrocarbons with functional groups, e.g., organic acids or alcohols, the measured values of the interfacial tension can be found considerably below the value of the hydrocarbon. This matter is illustrated in Table 1.

liquid	$\sigma_{l,g}$ [mN/m]	$\sigma_{l,H2O}$ [mN/m]
water	72,79	-
n-hexane	18,4	51,1
n-heptane	20,3	52,6
n-octane	21,8	50,8
benzene	28,9	34,96
Oleic acid	32,5	7,0
n-octanol	27,5	8,5

Table 1: Values of surface and interfacial tensions

At ambient conditions, i.e., standard pressure and room temperature, the interfacial tension between two liquids can be determined with the help of the Wilhelmy-Plate or the Du Noüy-Ring method. In case of highly volatile liquids the complete system has to be encapsulated in some sort of pressure chamber. This autoclave needs to be evacuated before the respective liquids enter and the measuring conditions are established. Then, determination of the wetting force becomes technically demanding since the sample liquids and the system for detecting the force are separated from each other. It becomes difficult to transmit the force for its determination e.g. gravimetrically. In addition, the material transport that occurs in extractive processes can only be defined and documented in an unsatisfactory manner.

In cooperation with the company KRÜSS GmbH the Eurotechnica GmbH has developed an apparatus based on the measuring method of the pendant, standing or sessile droplet [1], that allows measurements close to the operating conditions of liquid-liquid separation columns working in the droplet- and falling film mode. When joining two fluid phases within a pressure tight view cell, defined conditions regarding pressure, temperature and composition of the adjoining phases can be adjusted. The interfacial tension of the adjoining phases can thus be determined close to conditions of the actual process especially in dependence on their compositions.

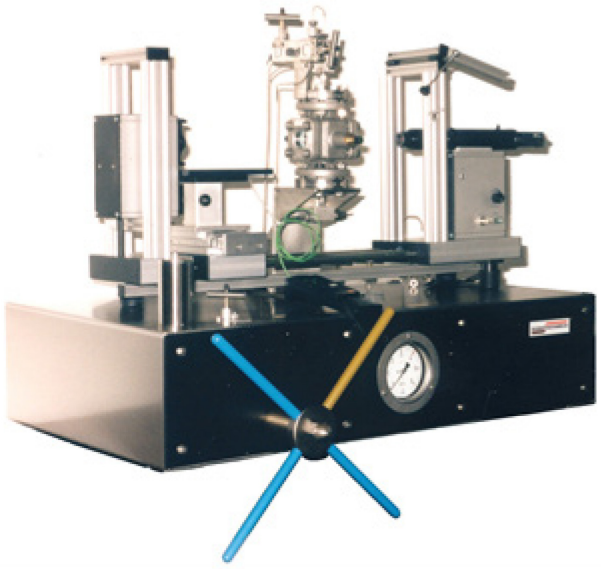

Fig. 1: PD–E40 for measuring interfacial tension and contact angle.

Figure 1 depicts the PD-E40 apparatus for investigation of liquid-liquid and gas-liquid systems, respectively, under pressures up to 40 bar. Besides determination of interfacial tension the volume of the view cell of the PD-E40 containing a relatively large high pressure window (optical view diameter 32 mm) is ready for investigation of wetting on solid surfaces like packing materials, e.g. in the case of mixtures of volatile hydrocarbons at elevated pressures. A number of examples for application are listed in Table 2.

technical application	drop phase	surrounding phase	typical range of temperature and pressure
fine chemicals	aqueous phase + transfer component	organic phase + transfer component	5 – 20 bar, 40° bis 120°C
petro-chemistry	bitumen, asphaltenes	Aliphatic and aromatic compounds (Xylenel)	30 bar, 180° C
lubricants (emulsions)	water	organic phase	3-5 bar, 180° C
absorption, washing towers	water + additives	CO_2, H_2S	1 – 10 bar, 20° C
food technology	edible oil fraction	solvent	vacuum (to 5 mbar) up to 80° C
refrigeration technology	transmission oil	tetrafluoroethane (R134a), propane	1 – 40 bar - 30° bis 40° C
distillation, rectification	alcohol volatile organic solvents	vapour phase	50 mbar – 1 bar 60° bis 80° C
coating technology	glue	solvent (water, hexane, benzene)	1 bar, 20° C

Table 2: Technical applications for measurement of interfacial tensions.

Experimental procedure

Initially, the phase of the droplet has to be chosen according to the application and the ratio of the densities. In case of the drop phase being the lighter one, the method of the standing drop has to be applied. Photos exemplifying the methods of the pendant, standing and sessile drop are depicted in Figure 2. They allow determination of the interfacial tension by means of corresponding software for drop shape recording and analysis, e.g., DSA from KRÜSS GmbH. The pressure of the phase surrounding the drop has to be applied externally (gas reservoir, pump etc.). Alternatively a second piston system can be integrated into the measuring apparatus. From the contour of the drop, information like interfacial tension, wetting properties

and temporal changes, e.g., of volume or interface can be obtained [2].

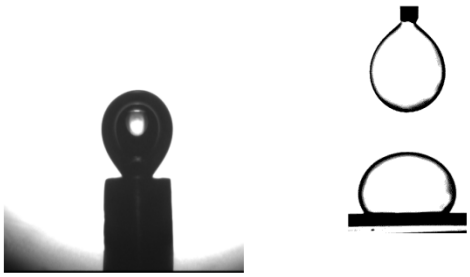

Fig. 2: standing bubble, pendant and sessile drop.

Example: fractionation of triglycerides

During treatment of edible oils and fats, e.g., for the production of desired fractions of fatty acids after hydrogenation, falling film evaporators are used. They are operated under vacuum in order to work under relatively mild temperature conditions. The heat transfer necessary for evaporation is determined to a large extent by wetting and the possible formation of trickles. The tendency for improved wetting under vacuum conditions increases in case of decreasing surface tension. As an example figure 3 depicts the surface tension of a fraction of triglyceride oil in vacuum at various temperatures.

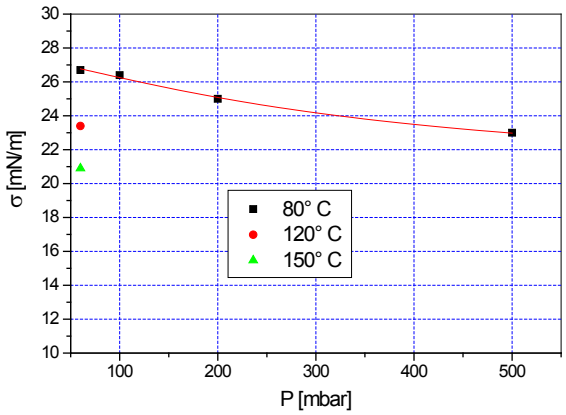

Fig. 3: Surface tension of a fraction of triglyceride oil under vacuum.

Example: liquid – liquid extraction

Performance of separation columns depends to a large extent on the wetting of packing surfaces inside the column, drop size distribution and phase separation. Besides the difference in density the interfacial tension is an important system parameter that contains information with regard to the possibility of dispersion and back mixing. In case of differences in density of more than 500 kg/m^3 and interfacial tensions larger than 20 mN/m additional devices for dispersion have to be installed (rotating plates, paddles, etc.). On the other hand these values can vary considerably from the head of the column towards the bottom, which may indicate required energy input for dispersing initially but a phase separation problem somewhere else. Hence, determination of the actually prevailing interfacial tension is of importance and has to be carried out under process conditions.

In case of the extraction of an organic acid samples of the aqueous and the organic phases from the head as well as from the bottom of the column were brought into contact (90–125 °C, 3-6 bar) using the method of the pendant drop under process conditions in the apparatus described before (Figure 1). In order to determine the interfacial tension the dispersed phase should be chosen as the drop phase for the measurements. While the differences in density turned out to be within the same order of magnitude, a threefold increase of the interfacial tension was measured at the bottom of the column in comparison with the top of the column. The overall low values of the interfacial tension between 2 and 6 mN/m as well as of the difference in density of 120 kg/m^3 cause enhanced axial back mixing as well as a diminished separation efficiency of the column. Moreover, one of the two phases is the better agent for the wetting of packings inside the column. As the phase to be dispersed into a number as large as possible of small droplets, the one with the inferior wetting properties has to be chosen consequently.

Summary

The measuring apparatus PD-E40 is an instrument universally applicable for the measurement of interfacial properties in liquid-liquid and gas- liquid systems. It allows determination of parameters of relevance to liquid separation tasks close to process conditions. It is an important tool for design and operation of corresponding industrial plants.

References

[1] Andreas, J.M., Hauser, E.A., Tucker, W.B., J. Phys. Chem., 42 (1938), 1001-1019.

[2] Jaeger, P.T., R. Eggers, H. Baumgartl, J. Supercrit. Fluids, 24 (2002), 203-217.

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