Development of tools for supercritical fractionation modeling: preliminary measurements of interfacial tensions and contact angles

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Supercritical CO_2 fractionation is a separation process for liquid mixtures, which offers the advantages of being able to be conducted continuously, at low temperatures, with a selective and GRAS* solvent. These benefits open potential outlets for this process in many industries where the use of toxic solvents and high temperatures are not suitable anymore. However, supercritical CO_2 fractionation is not widely used in industry and requires the development of reliable tools for its scaling up in order to extend its application. Different types of modeling are used for packed columns that consider the thermodynamics of the involved phases as well as the hydrodynamics of the flows under pressure. However, some properties such as the interfacial tension (at the liquid/supercritical fluid interface) or the contact angle of the mixtures with the packing, are not always known under the operating conditions required for the implementation of supercritical CO_2 fractionation. In order to improve future modeling, interfacial tensions $\gamma_{L/F}$ at the liquid-supercritical phase interface and contact angles θ of the liquid phase in supercritical conditions were measured at equilibrium for ethanol-water systems. The choice falls on this mixture because its thermodynamic behavior is well known, and it has an industrial interest. The contact angles were measured on stainless steel supports, representative of the most used packings in supercritical fractionation columns. These measurements were carried out with a newly designed high-pressure and high-temperature experimental station including a high-pressure cell for the pendant or sessile drop methods to measure $\gamma_{L/F}$ or θ with stainless steel, respectively. The experiments allowed us to study the influence of the variation of three parameters, i.e., mass fraction of ethanol, pressure, and temperature as well as the nature of the stainless steel, on the interfacial tension and the contact angle. The studied mixtures had a mass fraction of ethanol of 0.25, 0.50 and 0.75. Pure water and pure ethanol were also studied. Pressures and temperatures were varied between 0.1 and 15.1 MPa, and 40 and 60 °C, respectively. Moreover, two different stainless steels, AISI 316 and AISI 316L, were characterized and investigated. The results showed that, at a constant temperature, the interfacial tension decreases with increasing pressure with values varying from 70 to less than 1 $mN.m^{-1}$ (fig.1a); conversely, the contact angle increases when pressure increases (fig.1b). The effects of temperature between 40 and 60 °C appear more limited and the results obtained with the two stainless steels are almost similar. Finally, the results showed that there is a perfect wetting of the stainless steel by ethanol, unlike water which forms angles comprised between 65 up to 130 ° depending on pressure and temperature. For a given pressure, the addition of ethanol in the solution greatly modifies the interfacial tension $\gamma_{L/F}$ which tends towards the pure ethanol behavior, as well as the wettability with a decrease in the contact angle θ.

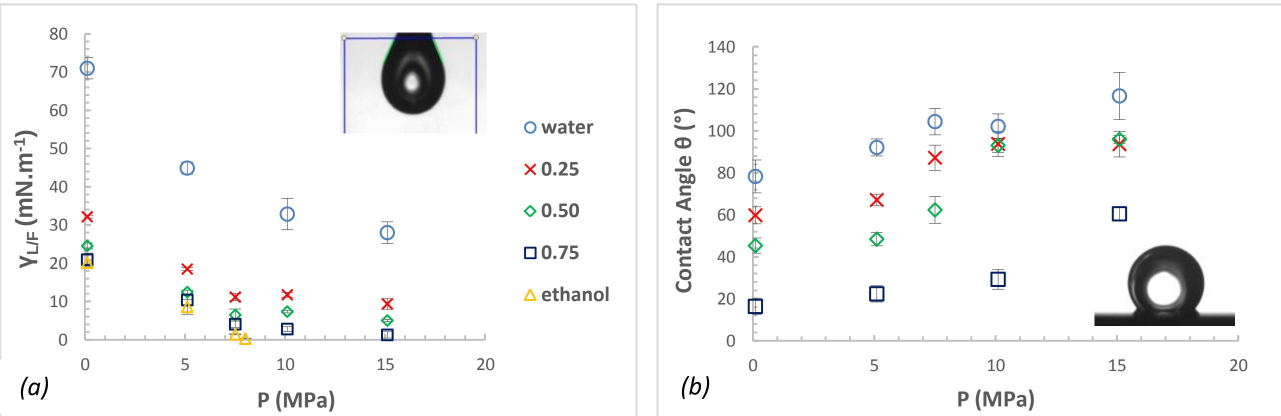

Figure 1: Evolution of (a) interfacial tension $\gamma_{L/F}$ and (b) contact angle θ on AISI 316 versus pressure at 40°C for different ethanol/water mixtures

* Generally recognized as safe (GRAS) is a United Food and Drug Administration (FDA) designation that a chemical is considered safe by experts.