

Preferential orientation and interfacial anomalous energies at interfaces in aqueous liquid-liquid solutions of molecular chains

E. Feria, J. Algaba, J. M. Míguez and Felipe J. Blas

Laboratorio de Simulación Molecular y Química Computacional,

CIQSO-Centro de Investigación en Química Sostenible and Departamento de Ciencias Integradas,

Universidad de Huelva, 21006 Huelva

The behaviour of liquid-liquid equilibria systems are an object of attention due to their participation in chemical processes, specially in petroleum industry. Fatty Acid Methyl Esters (FAMES) are very interesting compounds for being an alternative to fossil fuels, using them as biodiesel [1], and for their environmental applications, for instance, removing contaminants from water. On the other hand, hydrocarbons and alkanols produced in the industry act as contaminants because of their low solubility in water. In both cases, the interaction with water is controlled by the interfacial properties, which are the point of this investigation.

This work is focused on the comparison of the interfacial behaviour for mixtures solutions of FAMES with water and primary alkanols with water. On one hand, binary mixtures of primary alkanols, from 1-butanol to 1-heptanol [2], with water are studied at atmospheric pressure and temperatures between 280 K and 380 K. On the other hand, aqueous solutions of methyl esters, from methyl acetate to methyl heptanoate [3], are studied at atmospheric pressure and temperatures ranged between 278.15 and 358.15K. In both cases, the interfacial properties of the systems are obtained using molecular dynamic simulations (MD) [4] in the isobaric-isothermic or NP_zT ensemble with the direct coexistence technique. Density profiles, coexistence densities, compositions, and interfacial tensions obtained from simulations are compared with experimental data taken from literature.

Agreement between simulation predictions and experiments is good, including coexistence densities and compositions, as well as interfacial tension values. Molecular models are able to predict the characteristic parabolic shape of the interfacial tension as a function of temperature. They also capture the existence of a relative maximum value for each system at a temperature that increases as the molecular weight of the organic molecule is increased. Unfortunately, the experimental values of interfacial tension are substantially overestimated by our predictions in all cases. This is probably since unlike interactions between organic molecules and water are not accounted for properly.

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