

Surfactant-free CO₂-based Microemulsion

Robert F. Hankel[‡], Paula E. Rojas^{§#‡}, Mary Cano-Sarabia^{§#}, Santi Sala^{§#}, Jaume Veciana^{§#}, Andreas Braeuer^{‡*},
Nora Ventosa^{§#*}

[‡]Lehrstuhl für Technische Thermodynamik (LTT) and Erlangen Graduate School in Advanced Optical Technologies (SAOT) Friedrich-Alexander Universität Erlangen-Nürnberg. Paul-Gordan-Strasse 6, 91052 Erlangen, Germany

[§]Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB- CSIC), Campus la Universitat Autònoma Barcelona (UAB), 08193 Bellaterra, Spain

[#]CIBER-BBN: Campus Río Ebro - Edificio I+D Bloque 5, 1^a planta C/ Poeta Mariano Esquillor s/n, 50018 Zaragoza

ABSTRACT

Surfactant-free microemulsions are highly desired target in green chemistry. The presence of water-rich nanodomains in a pressurized, transparent, macroscopically homogeneous “water/acetone/CO₂” mixture was revealed by Raman spectroscopy. The nanostructure of this one-phase liquid system was also pointed out by its capacity to dissolve non-water and non-CO₂ soluble ibuprofen. This solubility behavior can be explained by the existence of “CO₂-expanded acetone” nanodomains, with small water content, able to dissolve this hydrophobic compound.

INTRODUCTION

Improving the poor solubility of polar materials is important for developing applications of compressed CO₂ (cCO₂). One of the most promising approaches for enhancing solubility in cCO₂ is to form microemulsions.[1] Microemulsions are macroscopically isotropic mixtures of at least a hydrophilic, a hydrophobic and an amphiphile component. Their thermodynamic stability and nanostructure are two important characteristics that distinguish them from ordinary emulsions.[2] In order to be more environmentally friendly, efforts are directed towards the formation of microemulsion with fewer amounts of green surfactants. Surfactant-free microemulsions have already been known since the late 70s, but only scarce papers deal with this topic. [3; 4] We have used Raman spectroscopy to have an insight at the molecular level of the effect of the addition of compressed CO₂ over a mixture of water and acetone, before the system separates in two liquid phases.

MATERIALS AND METHODS

Materials

Ibuprofen was purchased ((*RS*)-2-4-2-methylpropyl phenyl propanoic acid) from Fagron Iberica (Barcelona, España). Acetone, reagent Laboratory reagent; purity $\geq 99.5\%$ was supplied by Teknokroma (Sant Cugat del Vallès, Spain). The water used was mili-Q water, conductivity less than $0.2\mu\text{S cm}^{-1}$. Carbon dioxide (high purity SCF grade) was obtained from Carburos Metálicos S.A (Barcelona, Spain).

Methods

The dissolution of ibuprofen in the ternary system composed of water/acetone/compressed CO₂ was performed in a home-made high-pressure phase analyzer.[5].

RESULTS

In this work, we described for the first time, a surfactanless microemulsion with scCO₂ that exhibits a high capacity to solubilize a hydrophobic compound in the presence of water. [6] Interestingly, we found that when adding CO₂ to a mixture of water, acetone and ibuprofen, in

such concentration that the ibuprofen is precipitated, the system becomes more transparent upon the addition of CO₂ and a complete transparent single phase was observed at certain conditions of pressure and temperature. This increase in the solubility of ibuprofen in the mixture is very surprisingly as scCO₂ do not dissolve this compound[7]. However, it is well known that ibuprofen is very soluble in CO₂-expanded acetone.[8]. Acetone dissolves large amounts of CO₂. At contrary, water has insufficient ability to dissolve CO₂. [9] Therefore, this unforeseen behavior can be only explained if the mixture presents a certain structure at the microscopic level with well defined hydrophobic domains (CO₂ –expanded acetone) where the ibuprofen is dissolved and water rich domains. In order to confirm this hypothesis, we have used Raman Spectroscopy to have an insight at the molecular level of the effect of the addition of compressed CO₂ over a mixture of water and acetone. We have observed that the water molecules are more bonded with the addition of CO₂ in the mixture. Certain compositions of water, CO₂ and acetone and at certain conditions of pressure and temperature display the physical characteristics of microemulsions.

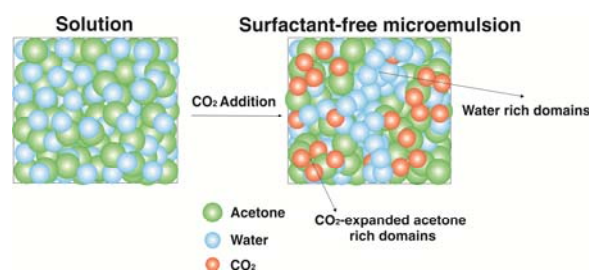


Figure 1: Formation of water-rich and water-lean regions is initiated by addition of CO₂ over a water and acetone solution at certain conditions of temperature and pressure.

CONCLUSION

A surfactant-free microemulsion can be formed by adding CO₂ to mixtures of water and an organic solvent with a high affinity for both of them. Raman spectroscopy is a useful technique to characterize the microenvironment of water molecules in this system. Surfactant-free CO₂-based microemulsions enable more environmentally friendly process routes.

REFERENCES

- [1] M. SAGISAKA, S. IWAMA, S. ONO, A. YOSHIKAWA, A. MOHAMED, S. CUMMINGS, C. YAN, C. JAMES, S. E. ROGERS, R. K. HEENAN AND J. EASTOE, *Langmuir* 2013, 29, 7618-7628.
- [2] C. STUBENRAUCH in *Microemulsions: Backgrounds, New Concepts, Applications, Perspectives.*, Vol. Wiley, 2009.
- [3] G. D. SMITH, C. E. DONELAN AND R. E. BARDEN, *Journal of Colloid and Interface Science* 1977, 60, 488-496;
- [4] M. L. KLOSSEK, D. TOURAUD, T. ZEMB AND W. KUNZ, *ChemPhysChem* 2012, 13, 4116-4119.
- [5] F. TEMELLI, A. CÓRDOBA, E. ELIZONDO, M. CANO-SARABIA, J. VECIANA AND N. VENTOSA, *Journal of Supercritical Fluids* 2012, 63, 59-68.
- [6] R. F. HANKEL, P.E.ROJAS., M. CANO-SARABIA, S. SALA, J. VECIANA, A. BRÄUER, N. VENTOSA., (manuscript submitted)
- [7] D. SULEIMAN, L. A. ESTÉVEZ, J. C. PULIDO, J. E. GARCÍA AND C. MOJICA, *Journal of Chemical & Engineering Data* 2005, 50, 1234-1241.
- [8] M. MUNTO, N. VENTOSA, S. SALA, J. VECIANA *Journal of Supercritical Fluids* 2008, 47, 147
- [9] P.G. JESSOP, B. SUBRAMANIAM, *Chemical Reviews* 107, 2007, 2666