Recent improvements in the high pressure differential calorimetry method applied to the study of gas hydrates

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Calorimetry and especially High Pressure Differential Scanning Calorimetry (HP-DSC) applied to the study of gas hydrates has originally been developed and patented (US6571604) by a collaborative work lead by the French Institute of Petroleum – New Energies. It was found to be a relevant tool for investigating the thermodynamics of formation and dissociation of gas hydrates as it is able to simulate the temperature and pressure conditions of their formation.

Originally applied to fields related to oil and gas production and flow assurance [1], then extended to the study of oil-water-gas systems and the emulsion stability of oils with hydrate [2], it has now been involved in several new studies. Indeed, carbon dioxide sequestration by CO_2/CH_4 exchange in natural gas hydrates present in marine sediments, carbon dioxide hydrates reversible formation/dissociation for refrigeration loops, hydrogen storage system through the formation of hydrogen hydrates [3], and many other studies involve the use of HP-DSC.

However, the technique still has some limitations which are linked to the fact that the gas hydrate formation in the calorimetric cell occurs at the gas-liquids interface. It leads to problems such as inefficient gas dissolution, long induction times, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, etc. Thus it makes for example difficult or impossible the accurate determination of heat capacities or of kinetics of formation/dissociation (except when water-in-oil emulsions are involved).

The presented work will cover these new fields of application of the technique and will include the description of a new high pressure, mechanically stirred calorimetric cell which overcomes the existing limitations. This cell has been developed by the Laboratory of Complex Fluids and their Reservoirs of the University of Pau and Pays de l'Adour (patent #FR/2012/57319 UPPA-CNRS) and has been industrialized and commercialized by SETARAM Instrumentation.

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[3] W. Weselowski, A. Kartuj, F. Laam, *J. Therm. Anal. Calorim.*, 81 (2008) 1237.