



## Investigation of phase behaviour of selected chemical reaction mixtures in microemulsions for technical applications



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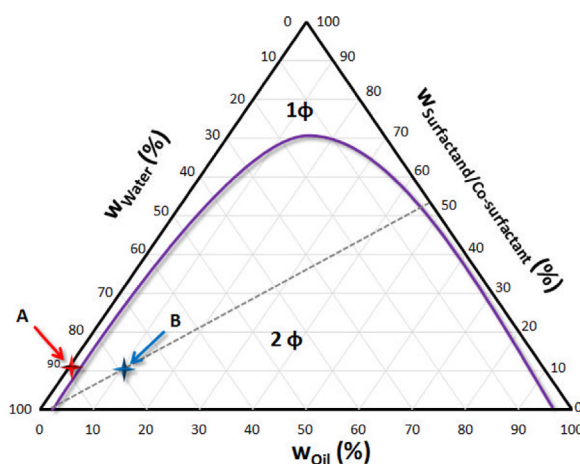
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### HIGHLIGHTS

- Phase behaviour for catalytic reactions in microemulsion systems is investigated.
- In hydroformulation reactions, phase boundaries are shifted during reaction.
- In Heck reactions, one-phase systems are possible at low reactant concentrations.
- High inorganic base concentrations lead to two-phase systems.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The phase behaviour of microemulsion systems, which are used as reaction media for hydroformulation and Heck coupling reactions, is investigated. A detailed analysis of microemulsion systems is the key for a successful implementation in technical processes. In the case of the hydroformulation reaction, the desired three-phase state is shifted depending on the composition of the reaction mixture and a temperature profile is required to maintain this state during the whole reaction. In case of the Heck coupling reaction, the desired state is an oil-in-water (o/w) one-phase microemulsion. We found that the best reaction performance is with  $K_2CO_3$  as the base, but at higher reactant concentrations with the same base only two-phase systems are obtained. Heck reaction was successfully performed at higher reactant concentrations in the two-phase system consisting of >75 wt% water. The applied heterogeneous sol-gel supported palladium catalyst could be easily recycled with minor catalyst leaching.

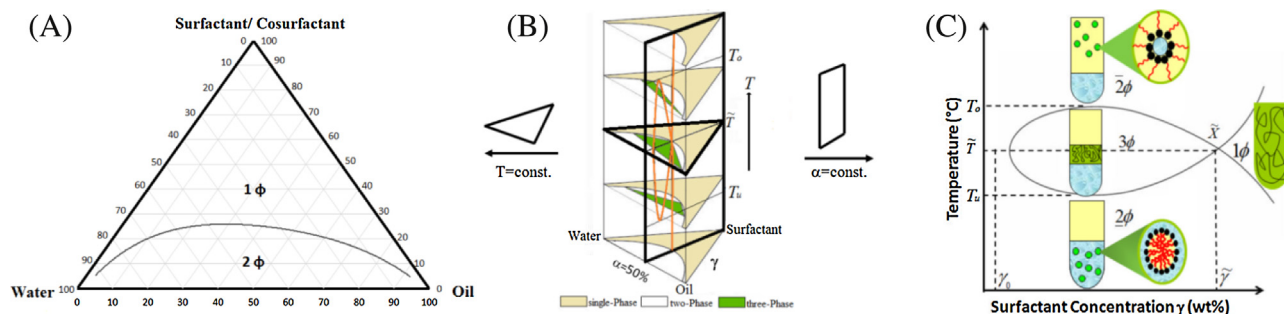
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### 1. Introduction

Surfactant-based reaction media are increasingly the subject of both fundamental and industrial research [1–9]. Microemulsions are clear, thermodynamically stable mixtures of oil, water and

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**Fig. 1.** Schematic phase prism of a ternary oil–water–nonionic surfactant system (B) and the  $T$ - $\gamma$ -diagram for constant  $\alpha = 50\%$  (C) as well as the ternary triangle diagram for constant temperature (A).

surfactant, which increase mutual the miscibility of hydrophobic reactants (oil) and water as an environmentally and user-friendly solvent [10]. Due to the properties of microemulsions, more environmentally friendly processes can be realized by reusing of catalysts and solvents [11]. The recycling of the valuable noble metal catalysts is crucial for the economic feasibility of an overall process as well. Catalytic reactions in substrate–surfactant–water systems make it possible to capitalize on these advantages and surfactant-based reaction media have been applied successfully for a variety of homogeneously catalysed reactions [12–16]. However, due to the complex nature of microemulsions, there are some challenges with the application of microemulsion systems, especially if continuous processes are targeted. For hydroformulation and Heck coupling reactions that are issued in this paper, two common problems are prevalent. First of all, due to the stability range of microemulsions, only very low reactant concentrations (10–100 mmol/L) can be used [17]. Secondly, product isolation has not been studied adequately. To take advantage of microemulsions on a technical scale and to ensure the isolation of the product and subsequent reuse of the catalyst, it is necessary to study these systems in detail. Especially, the knowledge of the phase behaviour and the phase separation dynamics are important information, which is needed to ensure a stable separation procedure within a process [18]. A process where the microemulsion system is only optimized for the reaction will be highly inefficient, if this system is further treated in conventional manner in the downstream process steps.

The phase behaviour of ternary micellar systems strongly depends on the temperature and the composition of the mixture. The complete phase behaviour is represented by the Gibbs phase prism as shown in Fig. 1(B). Usually the knowledge of the whole phase prism is not needed for process development and depending on the individual task; the use of defined sections is more appropriate and allows for simplification. For a constant oil-fraction, the  $T$ - $\gamma$ -section is used to describe the phase behaviour (Fig. 1(C)). For nonionic surfactants, at low temperatures and low surfactant concentrations an oil-in-water (o/w) microemulsion is in equilibrium with an organic excess phase. This two-phase region is called Winsor I-system or  $2\Phi$ . The surfactant transfers gradually from the water-rich phase to the oil-rich phase as temperature increases. At high temperatures the surfactant is better soluble in the organic phase and forms a water-in-oil (w/o) microemulsion which is in equilibrium with a water excess phase. This situation is called Winsor II-system or  $\bar{2}\Phi$ . Above a certain surfactant concentration ( $\tilde{\gamma}$ ) a macroscopically single phase microemulsion is formed, which is called Winsor IV-system or  $1\Phi$ . At intermediate temperatures and lower surfactant concentrations, a three phase system (Winsor III-system or  $3\Phi$ ) is obtained, where the middle phase is the microemulsion that coexists with an excess water and oil phase [19]. The so-called  $\bar{X}$ -point given by  $\tilde{\gamma}$  and  $\tilde{T}$  (phase inversion temperature (PIT)) is the intersection of the 3-phase and 1-phase

region, which marks the minimum mass fraction  $\tilde{\gamma}$  of surfactant needed to solubilise water and oil at the corresponding temperature  $\tilde{T}$ .

For ionic surfactants  $\bar{2}\Phi$  and  $2\Phi$  switch their position due to their increasing solubility in the aqueous phase with increasing temperature [20].

The formation of microemulsions with non-branched, ionic surfactants, such as hexadecyl-trimethyl-ammonium bromide (CTAB), requires the addition of co-surfactants, usually a short or medium-chain alcohol such as 1-propanol, which help to stabilize the micellar structures. Important parameters to characterize a microemulsion system are the weight fractions  $\alpha$ ,  $\gamma$  and  $\delta$  [Eq. (1)]. In Eq. (1)  $m_{\text{oil}}$  is the mass of oil,  $m_{\text{water}}$  is the mass of water,  $m_{\text{surf}}$  is the mass of surfactant, and  $m_{\text{co-surf}}$  is the mass of co-surfactant.

$$\alpha = \frac{m_{\text{oil}}}{m_{\text{oil}} + m_{\text{water}}} \quad \gamma = \frac{m_{\text{surf}} + m_{\text{co-surf}}}{m_{\text{oil}} + m_{\text{water}} + m_{\text{surf}} + m_{\text{co-surf}}}$$

$$\delta = \frac{m_{\text{co-surf}}}{m_{\text{surf}} + m_{\text{co-surf}}} \quad (1)$$

The  $T$ - $\gamma$ -section is a useful tool to study the temperature dependent phase behaviour as a function of the surfactant concentration, but there are limitations. If the phase behaviour should be studied at different compositions, thus  $\alpha$  and  $\gamma$  are varied, the  $T$ - $\gamma$ -diagram fails. In such a case, the ternary triangle diagram as schematically shown in Fig. 1(A), obtained at a constant temperature, is more appropriate. With the knowledge of the “tie-lines”, it is also possible to know the composition of the phases after phase separation, which is needed for the separation process design.

In this contribution, we investigate the phase behaviour for two important reactions: (a) hydroformulation and (b) Heck coupling reaction. The hydroformulation of olefins (Fig. 2) is an industrially important reaction for the production of linear aldehydes. In the Ruhr-Chemie/Rhône-Polenc-Process (RC/RPP), hydroformulation of 1-propene to *n*-butanal is carried out with a water-soluble Rh/TPPTS catalyst-complex and efficient separation of product and catalyst is achieved by a simple phase separation. A crucial requirement for the hydroformulation in this aqueous-organic two-phase media is the olefin solubility in water. While this prerequisite is fulfilled for 1-propene and 1-butene, it is not sufficiently given for long-chain olefins. The rhodium-catalyzed hydroformulation of long chain olefins, e.g. 1-dodecene, can be carried out under mild conditions by addition of nonionic surfactants as solubilizers [21,22]. The surfactants accumulate at the interface and thus reduce the interfacial tension.

In the hydroformulation of 1-dodecene in surfactant systems, a water-soluble rhodium complex (e.g. Rh/SX, SX = SulphoXanthphos) is applied which is present in the aqueous phase after reaction so that it can be easily separated from the hydrophobic product. From a technical point of view, the optimal

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