

# Adsorption at the liquid/liquid interface in mixed systems with hydrophobic extractants and modifiers

## 2. Dynamic interfacial tension at the hydrocarbon/water interface in binary mixed systems

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### Abstract

The dynamic interfacial tension for binary mixtures of hydrophobic metal ion extractants and a modifier were measured by using the drop volume technique. Four types of equimolar mixtures were considered: two chelating extractants: 2-hydroxy-5-nonylaceto-phenone oxime (HNAF) and  $\beta$ -diketone (1-phenyldecan-1,3-dion), two solvating extractants: trioctylphosphine oxide (TOPO) and tributyl phosphate (TBP), chelating and solvating extractants TOPO and  $\beta$ -diketone, and the chelating extractant HNAF and the modifier (decanol). With the aid of the Ward and Torday equation the values of the diffusion coefficients of individual compounds and their equimolar mixtures were estimated. It was found that in the case of two types of investigated mixtures, i.e., HNAF +  $\beta$ -diketone and HNAF + decanol the compound HNAF that was dominant in the mixed adsorbed monolayer and the more interfacially active also determined the kinetics of adsorption in mixed systems. In contrary to the mixture of two chelating reagents, in the case of a mixture of two solvating extractants the mixed system behaves like the less active, though dominant at the interface, reagent TBP. The same effect was observed in both of the considered diluents (toluene and octane).

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### 1. Introduction

Characterization of the dynamic behaviour of solute is of a great importance in a lot of applications. The modelling of adsorption of mixed surfactants is of a greater importance industrially because mixtures of surfactants rather than individual surfactants are used in many interfacial processes. In spite of that, relatively few studies concerning the dynamic surface tension of surfactant mixtures have been reported [1–4]. On the contrary, a considerable amount of work has been done on the adsorption kinetics of individual surfactants.

The process of liquid/liquid extraction of metal ions is a field where the dynamic properties of hydrophobic extractants are more important for determining the behaviour of the system than its equilibrium. For instance, in a real solvent extraction system, in a mixer–settler system the adsorption of molecules of an extractant as the first step of the metal ion complexation process occurs at the hydrocarbon/water interface which is continuously renewed. Therefore, there is a great need for research into the adsorption kinetics of extractants.

Moreover, for a new generation of solvent extraction systems consisting of a mixture of two extractants or an additional component, i.e., a modifier, research into the adsorption kinetics of a binary mixture of extractant/extractant or extractant/modifier type are of a greater importance.

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Several models have been proposed to describe the process of adsorption dynamics. When the adsorption process is diffusion controlled, one can use the approximation of the general diffusion equation of Ward and Tordai [5]. For the beginning of the adsorption process, the so-called short diffusion time approximation can be used:

$$\gamma_{t \rightarrow 0} = \gamma_0 - 2nRTc\sqrt{\frac{Dt}{\pi}}. \quad (1)$$

When the adsorption process is near equilibrium a long time approximation can be applied:

$$\gamma_{t \rightarrow \infty} = \gamma_{\text{eq}} + \frac{nRT\Gamma_{\text{eq}}^2}{c} \sqrt{\frac{\pi}{4Dt}}. \quad (2)$$

The parameters  $c$ ,  $\Gamma$ , and  $D$  represent the bulk concentration, equilibrium surface excess and monomer diffusion coefficient of the surfactant,  $n = 1$  for neutral molecules, and  $n = 2$  for ions,  $T$  is absolute temperature,  $\gamma_0$  is the interfacial tension of pure interface.

The values of the diffusion coefficient  $D$  can thus be obtained from dynamic interfacial tension measurements, depending on whether the adsorption process is in the initial stage or near equilibrium.

The purpose of this work was to study the adsorption kinetics in model extraction systems with a binary mixture of extractant/extractant and extractant/modifier type. Two types of extractants were considered: a solvating and a chelating one. Moreover, the influence of the type of organic diluent was studied. The short and long time approximation models of the Ward and Tordai equation were used to describe the dynamic interfacial tension of the individual extractant or modifier and the two-component mixture. The diffusivities of the investigated single systems and binary mixtures were estimated with the aid of these two equations.

## 2. Materials and methods

The methods of synthesis and purification of the investigated extractants were described in our previous paper [6]. Trioctylphosphine oxide (TOPO) from Sigma-Aldrich (analytical grade purity), tributyl phosphate (TBP) from Fluka (reagent grade purity), and decanol from POCh S.A. (analytical grade purity) were tested as received without further purification. Two types of organic diluents were used: toluene as a solvating hydrocarbon and octane as a non-solvating one, both purchased from Fluka. The hydrocarbons were distilled directly before the measurements. Redistilled water with a conductivity equal to 3  $\mu\text{S}$  was used as the aqueous phase.

The interfacial tension at the hydrocarbon/water interface was measured by the drop volume method with a TVT1 Lauda tensiometer (Germany). The dynamic interfacial tension measurements were carried out by the so-called “classical dynamic methods.” During the process, drops of the

aqueous phase were formed into the organic extractant solution at a constant flow rate. Variations of the flow rate caused changes in the detachment time ( $t_d$ ) which enabled the calculation of dynamic interfacial tension as a function of time. Keeping in mind that for investigated systems with surface-active compounds it is necessary to take into consideration that the detachment time ( $t_d$ ) is different from the age of the interface ( $t_{\text{ads}}$ ), the appropriate values of  $t_{\text{ads}}$  were calculated according to Eq. (3) described in the literature [7]:

$$t_{\text{ads}} = \frac{3}{7}t_d. \quad (3)$$

It is worth noting that in the case of the classical dynamic method which was used in the presented work, the area of the drop expands continuously during the adsorption process; in other words, the interfacial area is continuously renewed. Thus, in the case of the classical procedure the adsorption behaviour of an extractant and/or modifier molecules can be considered as being similar to adsorption at a newly created interface in a real liquid/liquid extraction system (for instance, in a mixer–settler system).

All measurements were performed at 21.0–0.1 °C in a temperature controlled cell. To avoid any transfer of solvent during the adsorption process all the experiments were performed by using mutually saturated organic and aqueous phases. The procedure of saturation, as described previously [6].

## 3. Results and discussion

Four model equimolar binary mixtures with the constant mole ratio of  $\alpha = 0.5$  in the bulk organic phase were investigated:

- mixture of two chelating extractants: 2-hydroxy-5-nonylacetophenone oxime (HNAF) and  $\beta$ -diketone (1-phenyldecan-1,3-dion);
- mixture of two solvating extractants: trioctylphosphine oxide (TOPO) and tributyl phosphate (TBP);
- mixture of chelating and solvating extractant: TOPO and  $\beta$ -diketone;
- mixture of chelating extractant HNAF and modifier (decanol).

### 3.1. Mixture of two chelating extractants (HNAF and $\beta$ -diketone)

The investigated mixture of two chelating extractants: HNAF and  $\beta$ -diketone can be treated as a system with chelating reagents and a modifier [8] that was described in detail in our previous paper [6]. Our earlier studies of equilibrium interfacial activity at the hydrocarbon/water interface for these two compounds revealed significant differences in the adsorption properties of HNAF and  $\beta$ -diketone.

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