Application Report

Diffusion coefficient of surfactants

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Calculation of Diffusion-Coefficients from the Maximum Bubble Pressure Experiment for Pure n-Alkyl-β-D-Glucosides

Since modern additives are usually active also in small concentrations, the performance of such substances is increasingly depending not only on efficiency and effectiveness as an absolute thermodynamic value, but also on speed.

The ability of surfactants to reach an interface within a given amount of time is defined by parameters of the surrounding phase. These are temperature, concentration, viscosity and so on, but to the largest extent the molecules' structure and size determine the ability to diffuse to and adsorb into/at the interface. These properties can be described by the molecules' diffusion and adsorption coefficients.

Depending on the concentration and the time range taken into account, one or the other process can be the rate determining step (rds).

At low concentrations and short times (usually < 100ms) the diffusion of molecules to the interface due to Brownian motion is the slowest step, so diffusion constants govern the performance of the additive. This is easily understood when imagine that only few molecules are near the freshly build interface, so reaching the interface by moving in an isotropic, Brownian manner is the rds.

Under these conditions the process of lowering surface tension in dependence of time is described in literature by Joos and Rillaerts [1].

$$\gamma_t = \gamma_0 - 2RTc\left(\frac{D_s t}{\pi}\right)^{0.5}$$

γ_t = interfacial tension at surface age t

γ_0 = interfacial tension of the pure solvent

R = universal gas constant

T = absolute temperature

c = concentration of the additive

D_s = diffusion constant for short times/small concentrations

Looking at high concentrations and long times (usually > 1s), the interface is already crowded with molecules, so it is difficult to penetrate the interface. In this case the adsorption at the interface is the rds. Ward and Tordai [2] developed a model describing the dependence of dynamic surface tension on the adsorption constant (diffusion constant for late times/large concentrations).

$$\gamma_t = \gamma_{eq} + \frac{RT\Gamma^2}{2c}\left(\frac{D_L t}{\pi}\right)^{-0.5}$$

γ_t = interfacial tension at surface age t

γ_{eq} = interfacial tension of the solution in mesoequilibrium (asymptotic value $\gamma_{(t)}$ approaches when $t \rightarrow \infty$)

R = universal gas constant

T = absolute temperature

Γ = equilibrium surface excess

c = concentration of the additive

D_L = diffusion (adsorption) constant for long times/high concentrations

Both models represent extremes. In reality a mixture of adsorption and diffusion usually governs the solution´s interfacial properties. These are best described by a model proposed by Rosen et al. [3] and applied by Tamura et al. [4], investigating foamability of surfactants. This semi-empiric formula fits dynamic surface tension data in a brilliant way, but does not allow calculating diffusion or adsorption constants.

$$\gamma_t = \gamma_{eq} + \frac{\gamma_0 - \gamma_{eq}}{1 + (t/t^*)^x}$$

γ_t = interfacial tension at surface age t

γ_{eq} = interfacial tension of the solution in mesoequilibrium (asymptotic value $\gamma_{(t)}$ approaches when $t \rightarrow \infty$)

γ_0 = interfacial tension of the pure solvent

t = surface age

t^* = surface age at the steepest point of the γ_t–t-curve

x = constant for a given additive (frequently around 0.5)

In this report the diffusion constants according to Joos and Rillaerts (early time, small concentration) of pure n-alkyl-β-D-glucosides (n-hexyl- to n-decyl-) from Anantrace Corp. are calculated from simple maximum bubble pressure experiments using a BP2-tensiometer. Table 1 shows the data of the samples.

	n-hexyl-β-D-glucosid	n-heptyl-β-D-glucosid	n-octyl-βb-D-glucosid	n-nonyl-β-D-glucosid	n-decyl-β-D-glucosid
concentration [mol/m^3]	1,02	1,00	0,88	1,03	1,00
molecular mass [kg/mol]	0,2644	0,2784	0,2924	0,3064	0,3204

Table 1: data of the samples

The experiments were carried out using distilled water as solvent at 293K. The data achieved are displayed in diagram 1.
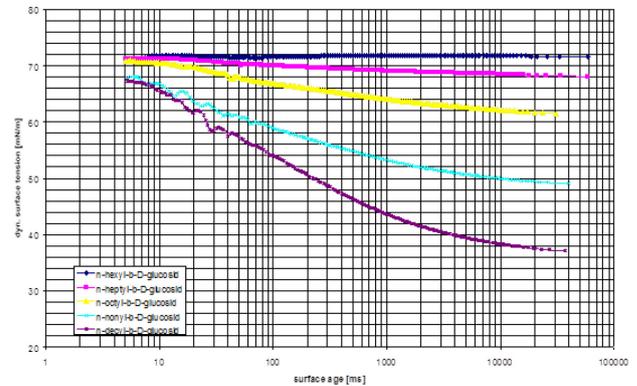

Diagram 1: dynamic surface tensions vs. surface age of n-alkyl-β-D-glucosides in water at 293K

When calculating the diffusion-constants according to Joos and Rillaerts and plotting them against surface age, one can decide whether or not this model is applicable to a specific time-frame. Diagram 2 shows diffusion-constants versus surface ages.
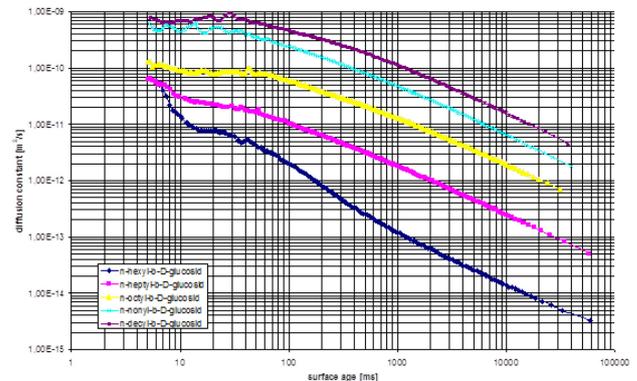

Diagram 2: diffusion-constants vs. surface ages of n-alkyl-β-D-glucosides in water at 293K

According to diagram 2 the diffusion-constants are only real constants in the surface age region below 100ms. The constants as physical values have been calculated taking surface ages from 10 to 50ms into account. At higher surface ages adsorption at the interface becomes more and more the rds. To determine the constants of adsorption (model of Ward and Tordai) the surface excess has to be known (e.g. by CMC-measurement). Table 2 shows the results for the early time approximation (Joos and Rillaerts model).

	n-hexyl-β-D-glucosid	n-heptyl-β-D-glucosid	n-octyl-β-D-glucosid	n-nonyl-β-D-glucosid	n-decyl-β-D-glucosid
diffusion-constant [m^2/s]	$\leq 7{,}30\pm2{,}18E^{-12}$	$2{,}14\pm0{,}61E^{-11}$	$8{,}51\pm0{,}45E^{-11}$	$4{,}69\pm0{,}66E^{-10}$	$7{,}50\pm0{,}81E^{-10}$

Table 2: diffusion-constants according to Joos and Rillaerts for of n-alkyl-β-D-glucosides in water

The data proof clearly that the diffusion-constants increase with increasing chain length of the hydrophobe. n-Decyl-β-D-glucoside is the fastest one regarding Brownian diffusion to the interface of all molecules investigated.

If the chain length increases over 10, the solubility of the n-alkyl-β-D-glucosides decreases dramatically, so the efficiency decreases.

The data are of a magnitude comparable to those published in literature for C12E6 (5.3-$8.4*10^{-10}$m^2/s), C10-dimetyl-PO 5-$5.5*10^{-10}$m^2/s), C12-dimetyl-PO (2-$5.9*10^{-10}$m^2/s) [1].

So the maximum bubble pressure method yields diffusion constants of surface active molecules in a very simple, easy and not much time consuming way. Since diffusion coefficients are true molecular values they are the tool to describe "speed" in a scientific manner.

Literature

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