Volatile aroma surfactants: evaluation of the adsorption-evaporation behavior under dynamic and equilibrium conditions

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Abstract

Multicomponent heterogeneous systems containing volatile amphiphiles are relevant to the fields ranging from drug delivery to atmospheric science. Presented here research discloses individual interfacial activity and adsorption-evaporation behavior of amphiphilic aroma molecules at liquid-vapor interface. Surface tension of solutions of non-micellar volatile surfactants linalool and benzyl acetate, fragrances as such, was compared with that of the conventional surfactant sodium dodecylsulfate (SDS) under equilibrium as well as under no instantaneous equilibrium, including fast adsorbing regime. In open systems, the increase of the surface tension on a time scale of ~10 min is evaluated using a phenomenological model. The derived characteristic mass transfer constant is shown to be specific both to the desorption mechanism and to the chemistry of the volatile amphiphile. Disclosed here fast adsorbing behavior, as well as synergetic effect in the mixtures with conventional micellar surfactants justify advantages of volatile amphiphiles as co-surfactants in dynamic interfacial processes. Demonstrated approach to derive specific material parameters of fragrance molecules can be used for an application-targeted selection of

volatile co-surfactants e.g. in emulsification and foaming, ink-jet printing, microfluidics, spraying and coating technologies.

INTRODUCTION

Surfactant mixtures are widely employed in industrial processing as well as in consumer products. Such technologies as coating, ink-jet printing, emulsification, detergency or foaming are based on a fast formation of a new surface (at time intervals of about milliseconds), so that the ability of surfactants to reduce surface tension under dynamic conditions defines the effectiveness of the whole process.[1-4]

The interfacial and evaporation behavior in mixed solutions of conventional and volatile amphiphiles, such as fragrances, are of especial interest because of their usage in home- and personal care products, e.g. in foams,[5-7] liquid detergents,[8] emulsions.[9]

However, the practical aspect of these earlier works aimed at olfactory trigger functionality, i.e. at relating the concentration of the volatile component in vapor phase to the composition of the interfacial layer or, more complex, to the non-ideality of the perfume-containing system.[9-12] In particular, evaporation paths of linalool from oil-in-water emulsion, stabilized with another surfactant, have been related to the emulsion phase diagram.[9] The release of fragrances from complex systems such as nanocapsules,[13] emulgels,[14] liposomes[15] or from cleavable surfactant profragrances[16] is usually assessed with (dynamic) headspace analysis in combination with mass spectrometry or with electronic nose.[17] In a series of papers, Penfold with coworkers have used Neutron Reflectometry to measure the rate of evaporation of the volatile component from the surface of mixed surfactant solutions, that allowed gaining valuable information on the time evolution of the composition of the mixed layer at the interface.[18, 19]

However, the use of classical equilibrium methods of colloid chemistry has led to a misapprehension of the effect of aroma molecules on dynamic interfacial processes. It is only recently, that individual interfacial activity[20-23] and fast-adsorbing behavior of aroma molecules[5, 24, 25] have been unveiled by measuring dynamic and equilibrium surface tension of individual and of mixed surfactant solutions. These studies indicated high potential of aroma amphiphilic molecules in dynamic interfacial processes. As example, it was shown that while on a long time-scale the composition of the interfacial layer is dominated by conventional surfactants as a result of desorption of volatile component, on a short time scale the wetting of surfaces by mixed

solutions reveals a non-trivial behavior. The spreading of a sessile drop can either be accelerated or retarded depending on the time scale of the process as well as on the concentration of the volatile component. [24] Importantly, these effects have been detected at a time scale of μs to s, much shorter than in the earlier studies on the wetting and evaporation dynamics of volatile binary sessile drops of e.g. water-ethanol solutions, also under variation of the ambient total pressure.[26-28] Presumably, in the case of poorly soluble amphiphilic aroma molecules their fast adsorption-desorption behavior leads to fast changes in the surface tension at air-liquid interface, dominating over possible effects of the environmental instabilities (temperature or humidity) on the wetting and evaporation of drops.

The most informative dynamic approach to study evaporation in systems with volatile amphiphiles is to saturate/evaporate pendant drops under certain conditions regarding concentrations in vapor and in bulk solution, temperature.[21, 29] This allows to eliminate additional solid-liquid interface and, accordingly, related interfacial processes. Through the variation of environmental conditions, it is possible to direct the fluxes and thus to trigger the instantaneous adsorption-desorption equilibrium at both sides (bulk solution and gas phase) of the interface. By modelling the dynamic surface tension with respect to the instantaneous composition of the interfacial layer, respective rate constants can be derived.[29, 30] Such methodological approach has been earlier applied in the studies of adsorption of short-chain alkanes from the saturated vapor on the surface of a water drop.[31] In this case the evaluation of the environmental impacts on the adsorption-desorption equilibrium at the gas-liquid interface is facilitated because of the elimination of the diffusion of the adsorbed molecules from the interface into the bulk of the drop.[32]

In case of water-soluble volatile amphiphiles such as short carbon-chain n-alcohols, energy barriers for desorption or re-adsorption at the gas phase have been shown to be dissimilar to that at the liquid side of the interface, with the adsorption from the gas phase providing a dominant contribution.[30, 33] In a recent study Danov et al. [21] reported an elegant study, when the surface of a pendant drop of pure water was saturated with aroma molecules in a closed atmosphere, resulting in a decrease of the surface tension of water up to a steady-state value. Then the droplet was allowed to evaporate. The resulting balance of fluxes to, from and across the air-water interface has been analyzed numerically using a detailed theoretical model. It was established that the

adsorption from vapors of linalool, benzyl acetate, and citronellol onto a water drop is barrier controlled. According to the determined kinetic constants, adsorption of linalool is several times faster, than that of benzyl acetate and citronellol. We note, that these results correlated with the vapor pressure of the studied fragrances, i.e. with the concentration of the volatile amphiphile in the subsurface volume. In the opposite case of evaporation from the droplet, the analysis of the underlying mechanisms led to a conclusion, that mass transfer dynamics is affected by the simultaneous evaporation of the solvent (water), which accelerates the desorption of benzyl acetate, while the desorption of linalool during the evaporation of the droplets is decelerated. However, the model reported by Danov et al.[21] requires the adjustment of a full numerical solution for each individual system. Therefore, searching for a simplified phenomenological analysis of the instantaneous changes in the composition of the interfacial layer during evaporation, with the minimum number of fitting parameters, should help to solve the "structure-property" relationship of volatile amphiphiles, as well as assist in selection of volatile surfactants for specific applications.

In this respect, studies on volatile amphiphiles with fast adsorption behavior require a combination of dynamic and equilibrium methods. Moreover, quantitative estimation of the evaporation rate can be used to gain a valuable material parameter for characterization and even prediction of the interfacial behavior of volatile amphiphiles, in addition to their known physicochemical properties such as solubility in water, vapor pressure, polarity.

In this paper we compare surfactant properties of linalool (LO) from the class of terpene alcohols, aromatic compound – benzylacetate (BA), both generally known as fragrances or aroma compounds, with the interfacial behavior of a conventional anionic surfactant sodium dodecylsulfate (SDS). Equilibrium, quasi-equilibrium and dynamic interfacial conditions have been modeled by pendant drop (in closed compartment and in open system), and maximum bubble pressure measurements. Special attention is brought to the consideration of instantaneous adsorption-desorption processes at both sides of the liquid-vapor interface related to the volatility of aroma molecules and to the comparison of the surface tension data derived at different time-scales/with different measuring methods. The evaporation kinetics of the pendant droplets under constant ambient conditions is described using phenomenological model approach, which takes

into account the evaporation flux. Fitting the experimental dynamic surface tension curves and application of equilibrium isotherms, allowed to evaluate a mass transfer coefficient as a material characteristic of the volatile solute for given conditions. Further, the presented results on the mixtures of conventional and volatile surfactants suggest that such aroma molecules can be used as co-surfactants to enable interfacial processes and to decrease the amount of residual surfactant in resulting products.

EXPERIMENTAL SECTION

Surfactants: Aroma compounds – linalool (LO), benzyl acetate (BA) and sodium dodecylsulfate (SDS) (all from Sigma-Aldrich), have been used as received. Relevant physical parameters of the substances are listed in Table 1. Critical micelle concentration (CMC) of SDS is 8.3 mMol/L.
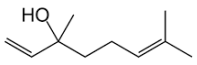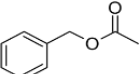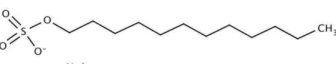
Dynamic surface tension was measured with maximum bubble pressure (MBP) method at 25 ± 0.5°C using a SITA pro line t100 apparatus (SITA GmbH, Germany) and a capillary from polyether ether ketone (PEEK) with an inner diameter of 0.8 mm. The pressure development in consecutively formed gas bubbles, formed at the tip of a capillary immersed into the liquid i.e. at fresh air-water interface, is monitored. A time window of the surface age ranges from tens of milliseconds to 20 seconds, allowing measurements of dynamic to quasi-equilibrium surface tension.

Pendant drop (PD) profile tensiometry has been utilized for the assessment of dynamic (time scale 1- 20 s) and equilibrium surface tension. Measurements have been done at 25 ± 0.5 °C and a constant humidity using horizontal microscope equipped with DCS-130 digital video camera. The value of the surface tension was determined from the drop shape analysis by numerical integration of the Young-Laplace equation and approximation of the resulting droplet shape to the experimentally obtained image. The drop volume was 10 μL.

To determine the equilibrium surface tension, droplets of surfactant solutions have been formed in a closed cuvette with a constant relative humidity (RH) of 100%, with a volume of ca 2.0 cm^3, filled in with an aliquot, 0.1 mL, of the solution with the same as the droplet concentration of the volatile surfactants in order to equilibrate the partial vapor pressures. To measure the changes of the surface tension during evaporation of the drops, they have been exposed to ambient air in the

laboratory with 40-50% RH, what leads to shifting the equilibrium towards continuous desorption of the volatile component into the gas phase.

Table 1. Parameters of the surfactants

Compound	Molecular formula	Structural formula	Mol. weight, g/mol	Solubility in water, mmol/L	Boiling point, °C	$\log P_{ow}$[a]	Partial pressure[b] mm Hg
Linalool	$C_{10}H_{18}O$		154.25	9.7	200	2.44	1.6
Benzyl acetate	$C_9H_{10}O_2$		150.18	20.6	212	1.96	0.18
SDS	$C_{12}H_{25}OSO_3Na$		288.37	8.3 (CMC)	n/a	1.6	n/a

[a] $\log P_{ow}$ – partition coefficient of an amphiphile in a two-phase system of n-octanol and water.
[b] At 25°C, PubChem substance and compound databases

Fitting of the experimentally measured data for the evaporation model

To link the time-dependent surface tension $\gamma(t)$, measured in the course of the evaporation of drops, to the bulk concentration, the equilibrium isotherm has been fitted with polynomial function in powers of $\ln(c,\text{mM})$, following the procedure proposed by Rehfeld[34]:

$$\gamma \ (\text{mN/m}) = A_4 \, (\ln c)^4 + A_3 \, (\ln c)^3 + A_2 \, (\ln c)^2 + A_1 \ln c + A_0 \qquad \text{(Eq. 1)}$$

This approach stems from thermodynamic reasons, and is based on the Gibbs' adsorption isotherm, therefore being independent from any model simplifications. The results of the fit are presented in Table S1 and in the graphical form in Figure S1 (Supporting Information).

The instantaneous changes of the drop volume $V(t)$ in the course of the evaporation have been derived by fitting data points, as obtained from drop shape profile analysis, with polynomial interpolation functions vs. time (Figure S2, Supporting Information).

RESULTS AND DISCUSSION

1. **Surface tension under dynamic and equilibrium conditions**

Surface tension of solutions of a conventional surfactant SDS and of two representatives of volatile amphiphiles - mono terpene alcohol linalool and aromatic alcohol ester benzyl acetate – has been measured using MBP tensiometry. Figure 1 a presents concentration dependences of the surface tension at 45 ms and at 20 s of the surface age, i.e. in a highly dynamic and in a quasi-static regime, respectively. Selected curves of the dynamic surface tension are displayed in Figure S3 a-c (Supporting information).
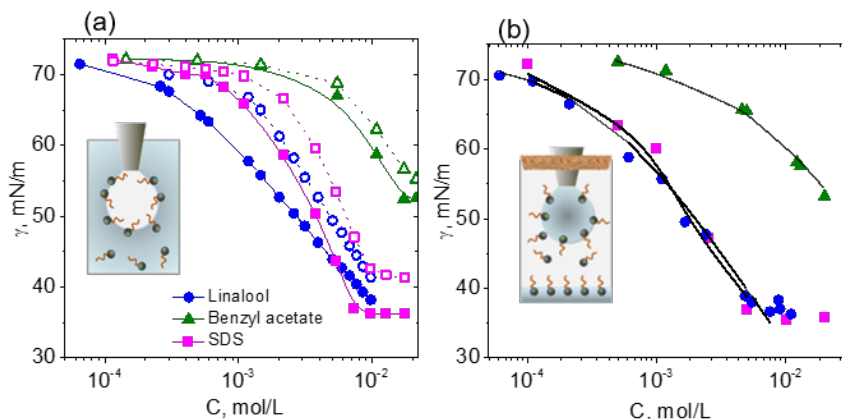

Figure 1. (a) Surface tension versus concentration in solutions of linalool (blue circles), benzyl acetate (green triangles) and SDS (magenta squares) measured at 20 s (filled symbols) and 45 ms (open symbols) of the surface age using MBP tensiometer. (b) Isotherms of the surface tension of SDS and volatile compounds (symbols as in a), measured with pendant drop (PD) method in a closed equilibrated cell.

SDS solutions exhibit a notable difference in the surface tension in dynamic (45 ms surface age) and in quasi-equilibrium (20 s) regimes even in the concentration range above CMC. (Figure S3 a, Supporting Information), while solutions of non-ionic volatile amphiphiles achieve a (quasi) time-independent surface tension on a time scale of seconds (Figure S3 b-c, Supporting Information).

As seen in Figure 1a, linalool possesses ahighinterfacial activity in millisecond range. Equilibrium conditions have been studied using PD tensiometry. In order to avoid evaporation of the solvent and of the volatile solute from the drop during the lapse time required to attain equilibrium adsorption, a sealed cuvette has been used. Before each measurement, the cuvette has been first equilibrated with an aliquot of the solution with the same surfactant concentration as the respective drop to be measured. This allowed to achieve fast adsorption-desorption equilibrium with the gas phase for both the solute aroma molecules and for the solvent

molecules. Figure 1 b presents equilibrium surface tension isotherms for three studied surfactants as well as their fits (solid lines) using Szyszkowski Equation (Equation 2).

$$\gamma_0 - \gamma = RT\,\Gamma_{max}\ln(1 + K_L\,c) \tag{Eq. 2}$$

where γ_0 is the surface tension of pure water at temperature T, R – universal gas constant, Γ_{max} denotes the maximum adsorption of surfactant at air/water interface, K_L is the Langmuir equilibrium constant (the ratio of the adsorption- to desorption rate constants).

In contrast to micelle-forming SDS solutions, the kink-point in the isotherms of the non-micellar volatile surfactants linalool and benzyl acetate is attributed to the limit of the molecular solubility (Table 1), which apparently correlates with the interfacial activity of the amphiphile substances. The comparatively low surface activity of benzyl acetate is probably due to its rather good solubility in water. However, we note, that this is not a general case for aroma molecules,[35] and clarification of this dependence requires further substances to be tested.

Knowing Γ_{max} allows assessing the area per molecule according to $S_1 = 1/(\Gamma_{max}\,N_A)$ (with N_A – Avogadro's Number). In order to compare the results of different measuring and evaluation methods, Table 2 presents adsorption characteristics estimated according to Equation 2, as well as data from earlier studies. Equilibrium isotherms and quasi-equilibrium surface tension data are displayed in Figure S4 (Supporting Information).

Table 2. Adsorption parameters evaluated from surface tension isotherms

Surfactant	$\Gamma_{max}{}^a \times 10^6$, mol/m^2	S_1, nm^2	CMC, mM *Solubility limit, mM	Source
SDS	3.2	0.53	8.3	Ref. [36]
	3.2	0.52	8.0	Present work
linalool	3.50	0.47		Ref.[20] (WP)
	5.66	0.30	10*	Ref.[21] (MBP)
	5.00	0.33		Present work
BA	4.63	0.36	20*	Ref.[21]

	4.84	0.34		Present work

[a] For linalool and benzyl acetate the theoretical values of Γ_{max} and S_1 correspond to maximum surface coverage at concentrations above the solubility limit.

Adsorption parameters of linalool evaluated in Ref.[20] are higher as compared to the values measured in the present study (Table 2). The discrepancy can be attributed to the difference in the exerted control over the adsorption-desorption equilibrium during the measurements. In WP method the composition of the interfacial layer is likely subjected to the instantaneous changes as a result of the evaporation of linalool from the relatively large air-liquid interface.

Comparison of the data from the present study with the evaluated parameters from Ref.[21] indicates a moderate consistency (Table 2), despite rather good agreement of the measured data points. The reason for the differences can be attributed to the fact in Ref.[23] van der Waals type of adsorption model has been used for the evaluation. Also Lewandowsky et al.[20] have shown that the evaluated data (area per molecule, interaction constant) for several perfume compounds vary depending on the theoretical equation used for the analysis of the measured data. These observations suggest that parameters determined in such way have only a limited significance; rather they can serve as empirical interpolation coefficients in a casual theoretical equation.

The evaluated parameters for SDS are in a good agreement with the literature data (Table 2).[36] The equilibrium isotherm of SDS is expectedly considerably shifted to lower values of the surface tension as compared to that measured with MPB at 20 s surface age (Figure S4 b, Supporting Information), indicating a slower process of attaining the adsorption equilibrium. Importantly, while equilibrium isotherms of SDS and linalool nearly coincide (Figure 1b), linalool exhibits a significantly higher dynamic interfacial activity (Figure 1a).

The above results indicate the possibility to determine both the dynamic behavior and the quasi steady-state adsorption of volatile amphiphiles in a single measurement using the high-throughput dynamic MPB method. Presumably, a small volume of the air bubble and low vapor pressures of most aroma molecules ensure a fast saturation of the gas phase, so that in this measuring geometry an instantaneous equilibrium can be assumed between the surface concentration and the concentration in each bulk phase at both sides of the interface. This is also

valid for the PD measurements in a saturated closed cell and explains, why the measured data can be well rationalized with classical model approaches, assuming no transfer of a solute through the interface into the gas phase. We note, however, that fast adsorption dynamics of volatile amphiphiles, with significant decrease of the surface tension happening in the μs range, cannot be satisfactory fitted with standard Ward-Tordai model.[24] Also, most of the reported evaluations of the dynamic data covered adsorption kinetics at a 1-100 s time scale, while reliable measurements of adsorption dynamics in μs range remain an experimental challenge[3, 37, 38].

2. Evaporation behavior of volatile surfactants

Adsorption of volatile amphiphiles in dynamic regimes both at short and at long time–scales is affected by transport processes at air-liquid interface from the bulk (water) to the surface, and from the surface into the gas phase. Therefore, we have compared kinetic curves of the surface tension measured with PD method under conditions which allow full equilibration (as in Figure 1b) and in open systems with no instantaneous equilibrium. Figure 2 displays dynamic surface tension of pendant drops with indicated concentrations of SDS (a, b), linalool (c, d), and benzyl acetate (d, e).
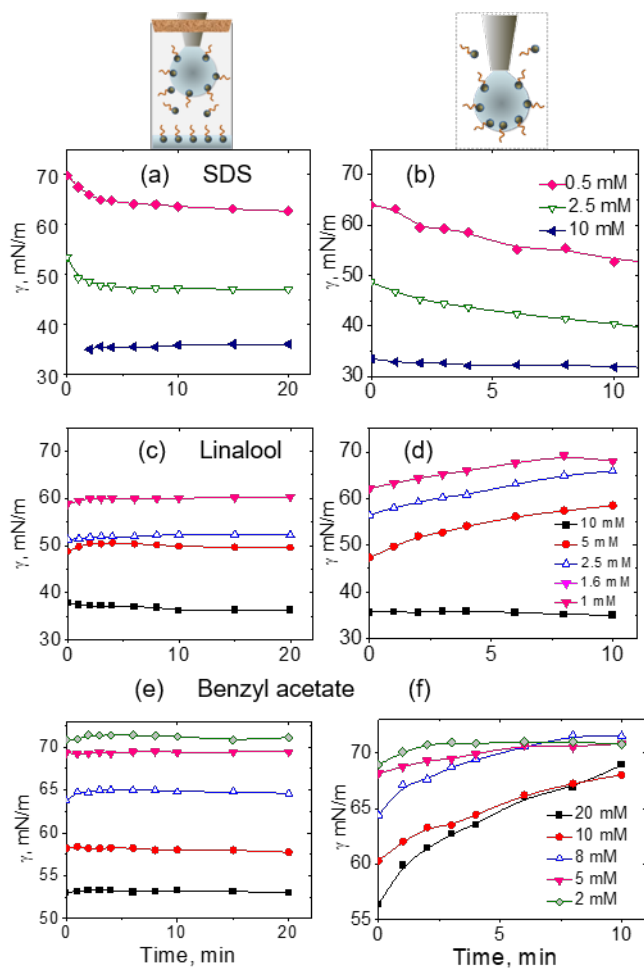
Figure 2. Kinetic curves of the surface tension measured with pendant drop method in a closed equilibrated cell (left panel), and in open cell (right panel), for SDS (a, b), linalool (c, d) and benzyl acetate (e, f) solutions with indicated concentrations. Symbols in the right and left columns correspond to the same concentrations as indicated.

Kinetic curves in closed systems confirm the static character of the PD tensiometric measurements, since on a time scale of seconds the surface tension becomes time-independent (Figure 2 a, c, e). Remarkably, in all studied cases the initial decrease of γ from 72 mN/m is too rapid in the first measured instants of time after the formation of the drop interface, so it can`t be monitored neither by the pendant drop method, no by dynamic MPB method (Figure S3, Supporting information). In the closed systems fine differences in the interfacial behavior of volatile and conventional surfactants are noticeable only in sub-minute range. The surface tension of SDS solutions drops down fast and retains at a constant value, while for the aroma molecules rather a small increase in γ is observed before the steady state value is reached.

A strikingly different behavior is exhibited in open systems which allow continuous exchange of the solution components with the atmosphere. For SDS solutions below the CMC (Figure 2b) the surface tension steadily decreases as a result of the reduction of the drop volume due to water evaporation. This leads to an increased concentration of the surfactant in the pendant drop.[24] For the solution with higher than CMC concentration, the surface tension is constant since the minimum value of the surface tension, and accordingly a maximum adsorption, has been attained at a time scale of sub-seconds.

As seen in Figure 2d, the surface tension of linalool solutions increases with time and for the diluted solutions almost reaches that of pure water within ~1000 seconds, so that the effect of the evaporation of the surfactant into the gas phase on the surface tension significantly overcomes the effect of water evaporation. Interestingly, the surface tension of linalool solution with 0.01 M concentration (close to the saturation limit) remains at a same constant value of 37±0.5 mN/m both in the closed and in the open system despite differences in the partial vapor pressures of the solvent and the volatile amphiphile in these systems. Presumably, in the open system the instantaneous changes in the volume concentration (and hence in the composition of the interfacial layer) due to the reduction of the drop volume and the evaporation of linalool proceed at comparable rates.

The surface tension of benzyl acetate solutions in the open system also increases with the evaporation time (Figure 2f). However, despite similar ambient conditions during the measurements, the changes in the surface tension of evaporating droplets of linalool proceeds with a constant velocity for different concentrations (parallel shift of the curves along the ordinate axis, Figure 2d), while the slope of the kinetic curves of the surface tension of evaporating benzyl acetate drops, i.e the changes in the composition of the interfacial layer, clearly depends on the bulk concentration. Furthermore, the surface tension of drops with 0.02 M of benzyl acetate (saturated solution) increases and almost approaches that of water on a time scale of 10 min, while the drop of the saturated linalool solution (0.01 M) has a constant surface tension, similar to SDS above CMC (Figure 2b). This observation confirms, that individual properties of aroma molecules, such as solubility, surface activity, $logP_{ow}$, and partial vapor pressure (Table 1), provide a dominant contribution to the changes of the surface tension during evaporation of droplets in open systems, so that the possible instabilities in the temperature or

RH of the environment can be neglected, to a good approximation. The effect from the variation of the solute concentration inside the drop as a result of the solvent evaporation can be taken into account explicitly, as shown in the next section. The quantitative assessment of the changes in the surface tension of evaporation drops is envisaged to provide material parameters which are specific to individual aroma molecules under given conditions.

3.   Evaporation model

Continuous evaporation of a volatile surfactant from the surface of a droplet into the air leads to a concomitant decrease of the local concentration at the interface and in its vicinity, which influences the surface tension. In case of water the evaporation kinetics was found to be consistent with a theoretical assertion that the diffusion transfer of the vapor through the boundary layer in the gas phase, adjacent to the water surface, is the rate limiting process.[39] Similarly to the treatment proposed in Ref. [39] here we adopt an „engineering" approach, and will neither consider the detailed concentration distribution nor solve the full set of diffusion equations, as it has been done in Ref.[21] Instead, the outflux of the volatile compound from the aqueous interface toward the ambient gas phase can be written as:

$$j_{gas} = -D_{gas} \frac{p_\infty - p_s}{L} \cdot \frac{1}{RT}$$

(Eq. 3)

Here D_{gas} is the diffusion coefficient, p_s is the partial pressure of the vapors of the volatile substance in the gas phase at a place which is directly adjacent to the physical interface, L is the effective characteristic thickness of the boundary layer, and $p_\infty \approx 0$ is the partial pressure far away from the surface. The feasibility of using the simplified approach described by Eq. (3) was confirmed in Ref. [40] where experiments demonstrated an existence of a linear concentration gradient of the evaporating species in a steady state.

If the diffusion transfer of the vapor through a boundary layer in the gas phase is the rate limiting process (Eq. 3), it is natural to assume that the local equilibrium between the interface and the sub-surface is established quickly both at the side of the aqueous solution, as well as with the interface-adjacent volume in the gas phase.[35] This assumption implies an absence of a local barrier for the exchange of molecules between the physical interface and the sub-surface. Therefore, the pressure p_s, the sub-surface concentration c_{sub}, and the adsorbed amount per unit

area, Γ, should be connected via equilibrium relationships. In particular, the Henry's constant K_H gives the proportionality between p_s and c_{sub}, stating that $c_{sub}=K_H \cdot p_s$. Now Equation 3 becomes:

$$j_{gas}=\frac{D_{gas}}{(RT) \, L \, K_H} \, c_{sub}$$

(Eq. 4)

One can envisage that the kinetic Equation (4), with the outflux being linearly proportional to c_{sub}, holds even in a more complex scenario when adsorption/ desorption barriers are also involved in the mechanism of surfactant transfer. Such a case was considered in Ref. [21], where the possibility for barrier desorption from the physical interface towards the contiguous gas phase was taken into account. That latter process was characterized by a desorption rate constant,

$k_{v,des}$, by stipulating that $j_{gas}=-k_{v,des}\Gamma f(\Gamma)$, Ref. [21]. As the volatile material comes

from the interface, the term $\Gamma f(\Gamma)$, which includes the adsorption Γ, stems from the surface chemical potential.[21] Under conditions of evaporation from a drop, intense convections in the aqueous interior would cause concurrent equilibration of the solute concentration inside the drop volume and with the interface, as discussed in Ref. [21]. Then, the adsorption isotherm is

applicable, in the form $Kc_{sub}=\Gamma f(\Gamma)/\Gamma_\infty$, where the function $f(\Gamma)$ refers to the van der Waals isotherm used in [21]. We now see that in this case, as considered in [21], the outflux

j_{gas} is also found to be linearly proportional to c_{sub}, similarly to Eq. (4), however with a

different multiplying coefficient, which includes $k_{v,des}$ and the adsorption parameters K, Γ_∞ from the aqueous side. Fast equilibration of the interface from the liquid phase is due to high dynamic interfacial activity of the volatile amphiphiles. Thus, the effective „resistance" of the interfacial layer can be represented by a constant coefficient in the relation $j_{gas} \propto c_{sub}$.

The requirement for mass conservation implies that the outflux j_{gas}, (Equation 4) leads to a decrease of the concentration in the aqueous phase (the drop), especially causing c_{sub} to diminish

with time. We stipulate that $\dfrac{dc_{sub}}{dt}\approx -j_{gas}/L_1$, where L_1 is a certain characteristic distance, and the total outflux includes also the transfer from the drop interior toward the sub-surface. A

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peculiar feature in this system is that the solvent (water) is also undergoing evaporation, and the related micro-convections in the droplet are known to facilitate the equilibration of the concentration in the bulk. The effect of convection–driven transport was discussed in Ref.[21]. In other words, the concentration c throughout the drop volume is in a chemical equilibrium with c_{sub}. This indeed will be the case if the convection (or diffusion) of the volatile substance in the bulk of the drop is faster than the process of evaporation, represented by the kinetic Equation 3. We note that a typical time scale of the changes of the surface tension due to evaporation is about 10 minutes (Figure 3), meaning that the changes in the composition of the interfacial layer occur slower as compared to the adsorption from the liquid phase (Figure 1). Therefore, a nearly uniform distribution of the surfactant in bulk can be assumed, so that $c_{sub} \approx c$. In view of the above considerations, Equation 3 acquires the form:

$$\frac{dc_{sub}}{dt} = -\frac{D_{gas}}{(RT) \ll_1 K_H}\, c_{sub} = -\,\alpha_{mt}\, c_{sub}$$

(Eq. 5)

Here the constant α_{mt} incorporates relevant physical parameters and has a meaning of mass transfer coefficient. Equation 5 is readily solved to yield:

$$c_{sub}(t) = c_{sub,0} \exp(-\alpha_{mt}\, t)$$

(Eq. 6)

where $c_{sub,0} = c_0$, a starting solution concentration.

As far as we assume a local equilibrium between the interface and the aqueous sub-surface, it is natural to accept that the instantaneous values of $\gamma(t)$ would correspond to the respective $c_{sub}(t)$, with c_{sub} at each instant expressed by the equilibrium isotherm. Then the isotherm in the form $\gamma(c_{sub})$ is combined with the function $c_{sub}(t)$ according to Equation 6 to give finally the predicted dependence $\gamma(t)$.

4. Verification of the evaporation model

In the following, the theoretical predictions will be verified by comparison with the experimental data. However, the model Equation 6 has also to account for the fact that the volume of the pendant drop decreases continuously with time as a result of the solvent evaporation. Applying

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an „engineering approach", we make a correction for the overall concentration of the volatile surfactant inside the droplet:

$$c_{sub}(t) = \frac{c_{sub,0} \, V_0}{V(t)} \exp(-\alpha_{mt} \, t)$$

(Eq. 7)

where $V(0) = V_{(t=0)}$. The drop shrinking is continuously monitored, so that the volume $V(t)$ of the drop can be easily evaluated using shape profile analysis. The obtained time dependence $V(t)$ is conveniently represented by fitting with polynomial interpolation functions (see Supporting Information). Combination of Equation 1, which describes $\gamma(c_{sub})$, with Equation 7 results in the theoretical $\gamma(t)$ dependence sought for. There is one adjustable parameter α_{mt}, which is found from interpretation of the experimental data, according to the following protocol: (i) a test value of α_{mt} is set; (ii) the time dependence of the concentration inside the droplet, $c_{sub}(t)$, is calculated from Eq. 7, using the interpolated experimental $V(t)$ for the given drop; (iii) the results for $c_{sub}(t)$ are substituted into the isotherm $\gamma(c_{sub})$, in its form of Rehfeld's type expansion, Eq. (1); (iv) the obtained function $\gamma(t)$ is compared with the measured data points, and the value of α_{mt} is corrected in appropriate direction, step (i).

Figure 3a displays experimental points) and respective fitting curves $\gamma(t)$ at three indicated concentrations of linalool. The changes of the drop volumes and respective fits (Table S2, Supporting Information) are shown in Figure 3b. It should be emphasized that all data sets are fitted with the same value of the mass transfer constant $\alpha_{mt} = 0.003425$ s^{-1} (or τ_{ev} $(1/\alpha_{mt}) = 292$ s), which has a physical meaning of characteristic time scale τ_{ev} of the evaporation process. This result suggests that the evaporation mechanism does not depend on the surface/bulk concentration, except for the most concentrated solution, when the surface tension grows slower than predicted by the model. We note that Danov et el.[21] for this concentration regime of linalool also observed a deceleration of its desorption during the evaporation.
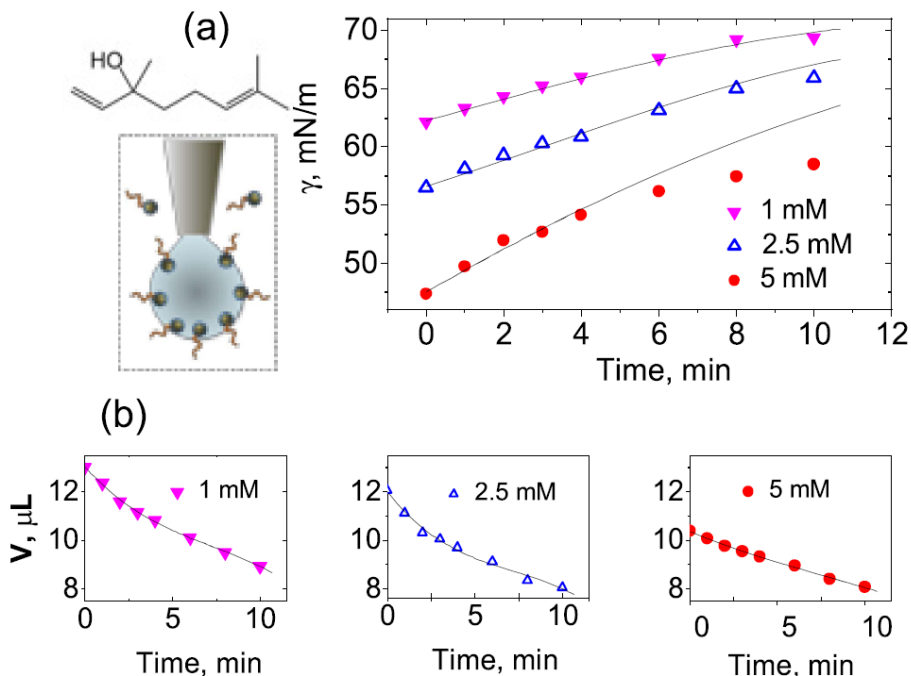
16

Figure 3. (a) Surface tension data from Fig. 3d and calculated curves according to Eq. (1) and (7) for linalool droplets with indicated concentrations. (b) Changes of the droplet volume $V(t)$ evaluated from the drop shape analysis. Solid lines are polynomial interpolation functions used in Eq. 7 (Table S2, Supporting Information).

Similar evaluation procedure has been performed with the experimental data on the evaporating droplets of benzyl acetate solutions (Figure 4 and Table 3). In contrast to linalool, the characteristic evaporation time of benzyl acetate depends on the starting bulk concentration of the drop. The higher the initial concentration, the faster is the evaporation of the volatile surfactant as seen in the decreasing values of τ_{ev} (Table 3). Although the analyzed drop bulk concentrations of benzyl acetate are higher than that of linalool (Figure 3 and 4), the interfacial adsorption is generally much lower in case of benzyl acetate (as follows from the surface tension isotherms in Figure 1). Presumably, in this concentration regime the effect of the interfacial adsorption on the rate constant k is more pronounced, than in case of a more dense interfacial layer of linalool

$$k = 1/\tau_{ev} \quad , \text{s}^{-1}$$

Another explanation can be attributed to large differences in the vapor pressure (Table 1). The retarded evaporation of linalool is, presumably, due to its high vapor pressure, so that the

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subsurface air volume next to the interface is crowded and "resist" evaporation. In contrast, the vapor pressure of benzyl acetate is 10 times smaller, so that the flux of the volatile into the gas phase is a less limiting process.
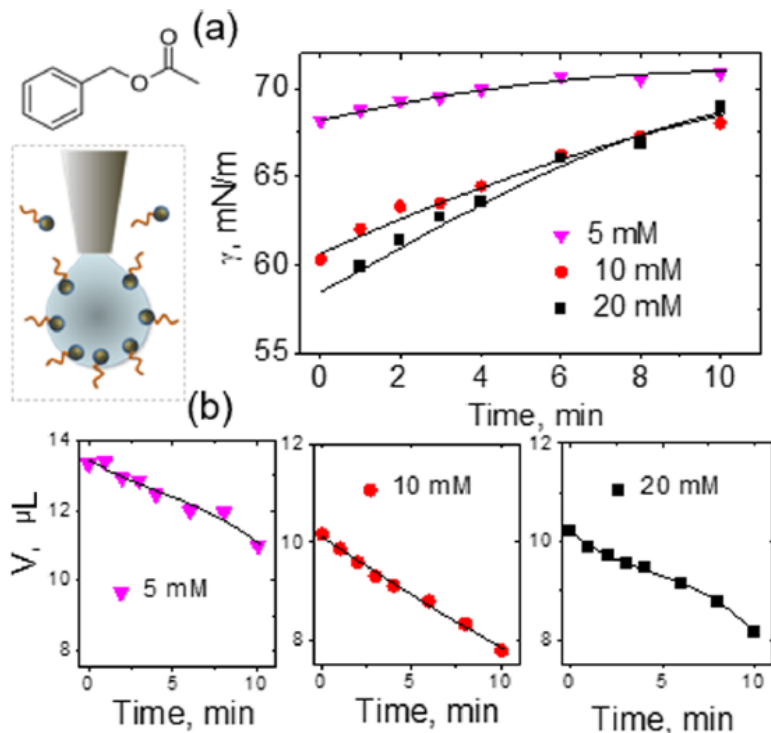

Figure 4. (a) Surface tension data and calculated curves according to Eq. (1) and (7) for benzyl acetate droplets with indicated concentrations. (b) Changes of the droplet volume $V(t)$ evaluated from the drop shape analysis. Solid lines are polynomial interpolation functions (Table S2, Supporting Information).

Table 3. Evaluated values of the evaporation constants of the droplets of benzyl acetate solutions

Initial concentration in the drop, mM	Relaxation time, $\tau_{ev,}$ s ($1/\alpha_{mt}$ in Eq. 7)	Evaporation rate α_{mt}, (Eq.7), s^{-1}
5 mM	462 s	0.002165
10 mM	420 s	0.002381
20 mM	355 s	0.002817

The above results confirm, that the simplified phenomenological model, which accounts for the evaporation of the volatile amphiphilic component and of the solvent, is capable to unveil both the differences in the evaporation mechanisms of two different amphiphiles as well as the

changes in the desorption process depending on the starting conditions. In particular, the effective evaporation of linalool from the interface of saturated solutions is retarded, possibly, because of molecular association as the solubility limit is approached. In contrast, the evaporation of benzyl acetate is presumably facilitated by the enhanced convection and the concomitant water evaporation. Reasons for this effect can be attributed to the molecular mechanisms of transfer - coupled fluxes of water and solute.

The validity of the model is further demonstrated by constructing master curves of the surface tension isotherms. To do that, the polynomials, which interpolate equilibrium isotherms for linalool and benzyl acetate (Figure S1, Equation 1) are combined with the experimental points of the evaporation measurements $\gamma(t)$, where the respective c_{sub} is evaluated according to Equation 7. As seen in Figure 5, the evaluated data perfectly overlap with the equilibrium isotherms.
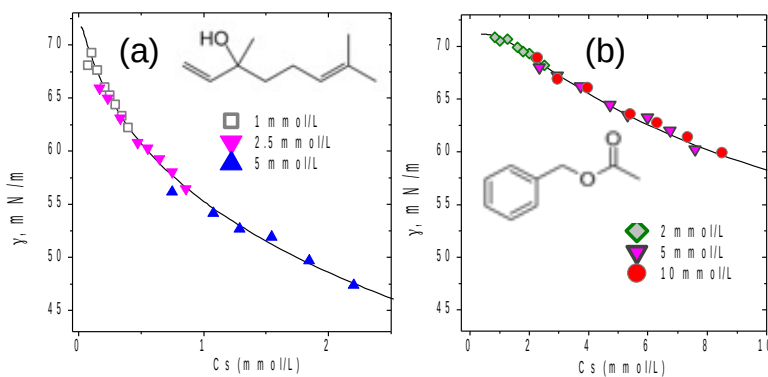

Figure 5. Master curves combining experimentally measured isotherms (represented by their polynomial fit according Eq. 1 and Table S1) and experimentally measured surface tension γ plotted versus evaluated c_{sub} from Eq. 7 for three independent droplet evaporation experiments for linalool (a) and benzyl acetate (b).

Although special care has not been taken to control the environmental temperature and humidity during evaporation of pendant drop {Portuguez, 2017 #94}, the local changes in the temperature of the boundary layer related to the enthalpy of water evaporation are limited to deviations in the surface tension of ±1 mN/m, comparable with the resolution of the tensiometry measurements (Figure S5, Supporting Information). These changes are much lower, than the effect of surfactant adsorption-desorption. We note, that although seemingly small, an increase of about 1.7-2.0 mN/m for γ in the open system (Fig. S5) as a result of water evaporation can be associated with a significant surface cooling effect of 5−10 °C.[46] Therefore, we would say that

our values of α_{mt} reported here refer to a local temperature of about 13−18 °C. These data are nevertheless consistent, as far as all experiments have been conducted under the same solvent evaporation / humidity and temperature conditions. The evaluated material transfer coefficient α_{mt} incorporates both environmental variations and transport mechanisms, specific for the volatile amphiphile.

To conclude, a good agreement between theoretical and measured time functions of the surface tension supports the validity of the main theoretical assumption, that the rate–determining stage in the evaporation process is the desorption and transfer of the aroma molecules from the air-water interface into the gas phase. These results also suggest that besides the intrinsic diffusivity and the surfactant concentration, also mass transport trough the interfacial layer as a result of evaporation considerably affects the surface tension of solutions of aroma molecules.

5. Dynamic surface tension of mixed SDS and benzyl acetate solutions

Depending on its composition and targeted application, each multicomponent surfactant system requires a specific choice of measuring methods and adjustment of experimental conditions with regards to the time-scale and concentration range. In particular, mixtures of nonionic fast-adsorbing aroma molecules and conventional (ionogenic) micellar-forming surfactants is an interesting model system with a significant applied potential. [24, 25, 41]

In the following we describe the interfacial behavior of SDS - benzyl acetate mixtures under dynamic conditions. Displayed in Figure 6a is surface tension, measured with MPB method, of SDS and benzyl acetate individual solutions, as well as of their mixtures with a constant fraction of benzyl acetate of 0.5 and 0.25 versus the total molar concentration of surfactants in solution. As clearly seen, partial substitution of SDS with less surface-active benzyl acetate has unproportionally small influence on the surface tension of the mixed solution. In the concentration range below the CMC of SDS, the dynamic behavior of the mixtures with a fraction of benzyl acetate of 0.25_{BA} is very similar to that of SDS solutions of the same concentration, while the surface activity of 50:50 mixture is slightly less surface active (Figure 6a).

It is generally known that mixed interfacial layer is typically enriched with a more surface-active component.[36] However, dynamic curves for selected concentrations in Figure 6b disclose that the short-term adsorbing behavior of SDS is enhanced in the presence of benzyl acetate.

Furthermore, around CMC of SDS a slight synergetic effect of the surfactants is seen in that the surface tension of the 0.25_{BA} mixture is lower than that of the individual solutions of each surfactant with the same concentration (Figure 6a). The synergetic adsorption behavior of mixtures of charged and non-ionic surfactants is typically attributed to the formation of a denser adsorption layer as a result of the reduced electrostatic repulsion of the charged head-groups.[36] In the mixed solutions studied here, the enhanced effective diffusivity of SDS from the bulk towards the interface is presumably due to the property of volatile surfactants to desorb from the interface into the gas phase thus effectively reducing the energetic barrier. We note that a strong synergetic effect has been observed in the mixtures of SDS with linalool,[24] the latter exhibiting a much higher than SDS dynamic interfacial activity.

From the practical point of view, employing mixtures of conventional and volatile surfactants is advantages in technologies, which require fast stabilization of creating interface at the initial stages of the processing, while the presence of surfactant in the final product is undesirable.
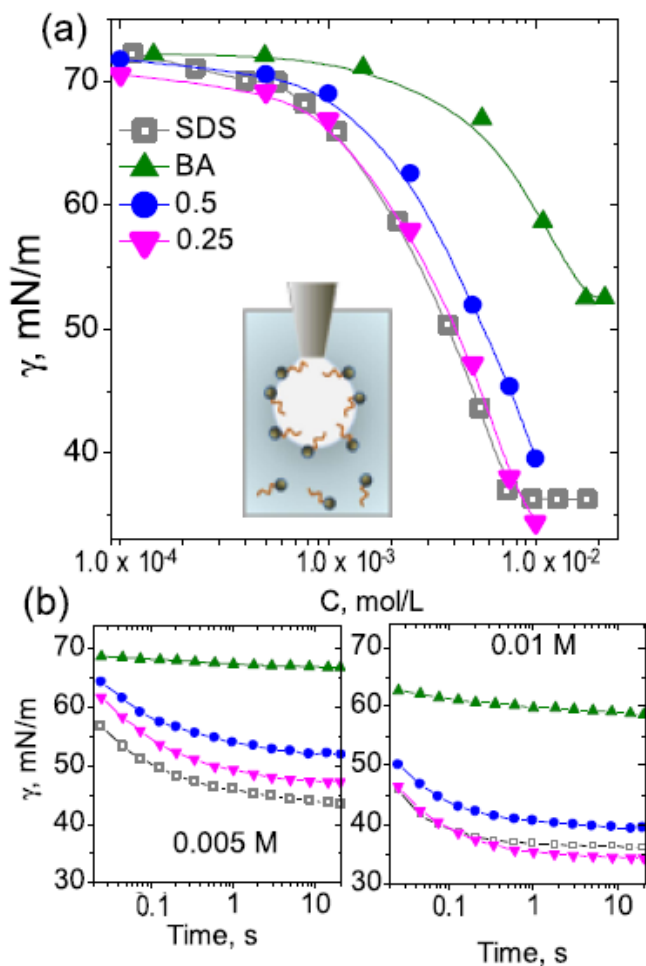
Figure 6. (a) Surface tension at 20 s versus concentration of SDS (empty squares), benzyl acetate (green triangles) and of their mixed solutions with a constant mole fraction of benzyl acetate of 0.5 (blue circles) and 0.25 (magenta triangles). All measurements have been done at 25°C. (b) Surface tension versus surface age for the selected solutions of SDS, benzyl acetate and their mixtures, symbols as in (a), with a total surfactant(s) concentration of 0.005 and 0.01 mol/L, as indicated.

Conclusions

This work reveals specific features of the interfacial adsorption-desorption behavior of volatile amphiphiles - linalool and benzyl acetate - in individual aqueous solutions, as well as in mixtures with conventional surfactant sodium dodecylsulfate. Surface tension has been assessed under equilibrium conditions as well as under non-equilibrium fast-adsorbing regimes with different measuring methods, including comparison with the earlier data.[20,21] Volatile amphiphiles demonstrate a fast-adsorbing behavior, so that with dynamic tensiometry - maximal bubble

pressure method - it is possible to asses in a single measurement both dynamic interfacial activity and quasi steady-state adsorption behavior on a time scale from ms to seconds.

In the regime of evaporation of a pendant drop (no instantaneous equilibrium conditions) at a time–scales of minutes the changes in the surface tension are defined by transport processes at both sides of air-liquid interface, in agreement with the earlier studies.[21, 29, 30, 33] It is shown, that the rate–determining process depends both on the individual properties and on the concentration of aroma substances.

The developed phenomenological model equation has been successfully tested against the experimentally monitored increase of the interfacial tension of evaporating droplets containing volatile amphiphiles. A single fitting parameter, mass transfer coefficient, encompasses full kinetic resistance of the interfacial zone and is specific both to the adsorption-desorption mechanisms and to the chemistry of the volatile amphiphile. These findings are in a good agreement with the results of a more complex numerical analysis.[21] The derived individual mass transfer constant - is envisaged to be used for the prediction of the interfacial behavior and, accordingly, for a targeted choice of volatile surfactants for specific applications

Revealed synergetic action of mixtures of conventional and volatile surfactants suggests promising applications of aroma molecules as co-surfactants in surface-emerging technologies, e.g. by providing fast dynamic activity and desorbing from the interface at later stages, thus decontaminating the final product, e.g. in ink-jet printing, emulsion polymerization, textile coloration, etc. We believe that consideration of specific interfacial behavior of volatile amphiphiles, disclosed here, is indispensable for understanding complex dynamic processes involved in, e.g. drying of films and evaporation of droplets, [18, 42, 43] stabilization of foams,[6, 7] formation of droplets in microfluidic devices [44] as well in phase separation of complex fluids.[45]

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: https://pubs.acs.org/doi/10.1021/acs.langmuir.1c02871?goto=supporting-info

Experimental and fitted with polynomial functions surface tension isotherms for studied surfactants; polynomial function for fitting of the drop volume changes with time (PDF);

comparison of the dynamic and static surface tension data and the effect of ambient conditions on the surface tension of evaporating water drop.

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TOC Graphic
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$$c_{sub}(t) = c_{sub,0} \exp\left(-\alpha_{mt}\, t\right)$$