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Volatile aroma surfactants: characterization of the interfacial behaviour at dynamic and equilibrium conditions

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Presented work discloses characteristic interfacial behavior of amphiphilic aroma molecules and justifies the advantages of their usage as surfactants and co-surfactants in dynamic interfacial processes [1,2]. Time-dependent surface tension γ of solutions of volatile compounds - a mono terpene alcohol (linalool), an aromatic alcohol ester (benzyl acetate), and of conventional surfactant sodium dodecyl sulfate (SDS) is shown to depend strongly on the chosen method (Figure 1).

At non-equilibrium conditions, aroma compounds demonstrate a high interfacial dynamic activity, i.e. an ability to decrease the surface tension of aqueous solutions at a time scale of milliseconds. Tensiometric measurements with pendant drop reveal that in open systems the adsorption-desorption at the liquid / air boundary is accompanied by evaporation, and the dynamic interplay of these processes defines the surface tension. A phenomenological model is developed and applied to account for the increase of the surface tension of the drop with time, γ(t), spanning the time range of ~10 min, which allowed to achieve a good agreement between theory and experiment. One adjustable parameter (material constant) is determined – the mass transfer coefficient of the volatile amphiphile across the water-air boundary.

Revealed synergetic behavior of volatile and conventional surfactants suggests revisiting numerous interfacial phenomena and processes which involve aroma molecules (perfumes), such as emulsion preparation, foam stability, spraying and cleaning.

Keywords: Volatile surfactants, dynamic surface tension, adsorption-desorption, evaporation

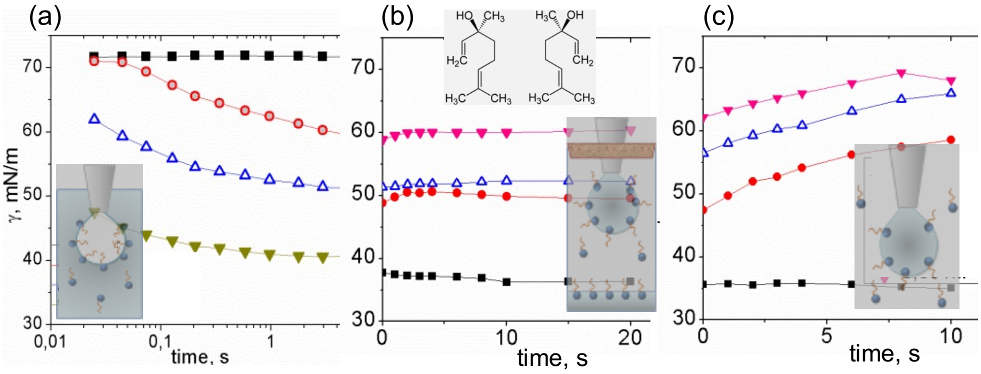

Figure 1. *Kinetic curves of the surface tension of linalool solutions measured using indicated methods. Solution concentrations (mM) from top to bottom: (a) 0, 10, 2.5, 7.5; (b-c) 1, 2.5, 5, 10.*

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References

[1] O.A. Soboleva, L.A. Tsarkova, Colloid J., 2020, 82, 437-447.
[2] O.A. Soboleva, et al. ACS Appl. Mater. Interfaces, 2019, 11, 40988-40995.

Volatile surfactants: characterization of the interfacial behavior at dynamic and equilibrium conditions

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Volatile Surfactants – Definition & Application Areas

Non-conventional volatile surfactants

- light amphiphilic compounds
- possess a distinct odour
- have low to negligible solubility in water
- e.g. synthetic perfumes, essential oils, terpenes

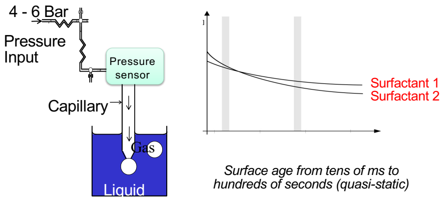
Quantified physico-chemical properties

- boiling temperature,
- solubility and partition coefficient $\log P_{ow}$

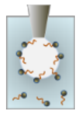
Challenge – to characterise and to link molecular structure to polarity, volatility, interfacial activity

Goal: Using facile and low cost static and dynamic tensiometry methods, we systematically evaluate surface activity and volatility of aroma molecules (volatile amphiphiles)

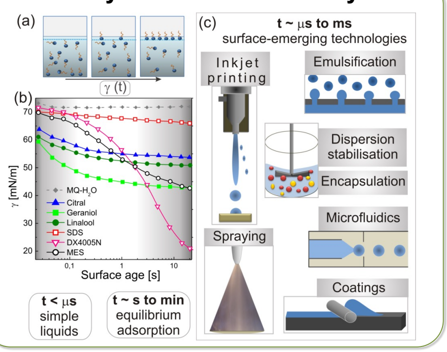
Bubble Pressure Tensiometry (MPB)



Amphiphilic molecules show differences in the dynamic adsorption behavior at interfaces depending on the concentration, temperature, molecular weight and molecular structure.



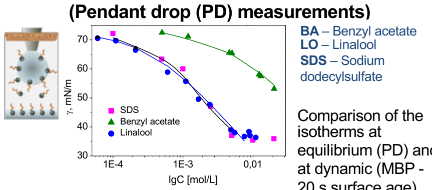
Dynamic surface activity



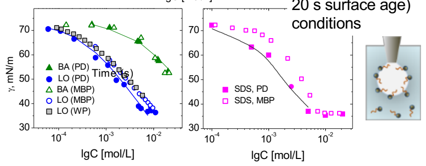
Volatile Surfactants – Synergetic Behavior with Conventional Surfactants

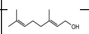
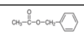
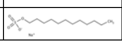
Surface tension isotherm

(Pendant drop (PD) measurements)

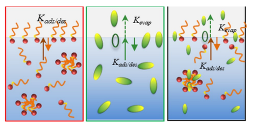


Comparison of the isotherms at equilibrium (PD) and at dynamic (MBP - 20 s surface age) conditions



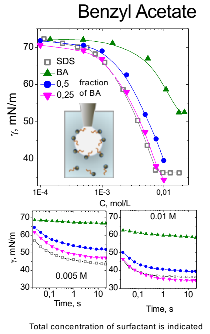
Compound	Molecular formula	Structural formula	Mol. weight, g/mol	Solubility in water, mol/L	Boiling point, °C	$\log P_{ow}$[a]	Partial pressu mm H
Linalool	$C_{10}H_{18}O$		154.25	9.7	200	2.44	1.6
Benzyl acetate	$C_9H_{10}O_2$		150.18	20.6	212	1.96	0.1[illegible]
SDS	$C_{12}H_{25}OSO_3Na$		288.37	8.3 (CMC)	n/a	1.6	n/a

- Volatile amphiphiles act as co-surfactant at air-water interface
- Dominant adsorption of volatile amphiphiles at air-water interface at low surfactant concentrations and at short time-scales



Mixtures of SDS with:

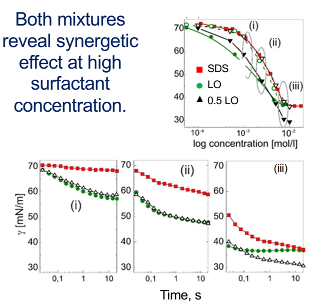
Benzyl Acetate



Total concentration of surfactant is indicated

Both mixtures reveal synergetic effect at high surfactant concentration.

Linalool



Evaporation Behavior

Phenomenological Model

Theory – main assertions:

p_0 – partial pressure of LL in the bulk of gas ≈ 0;

p_s – at the interface (from the gas side), $p_s = K_H . c_s$

K_H – Henry's constant (local equilibrium between vapor and water at c_s)

Assumption: insignificant diff. flux from the drop interior toward the sub-surface.

σ depends on time due to its connection with $c_s(t)$, that is, $\sigma(t) = \sigma[c_s(t)]$

➢ We combine the predicted $c_s(t)$ with the established $\sigma(c_s) = \{\sigma(\theta) \,\&\, \theta(c_s)\}$ – the „isotherm", to draw the theoretical dependence.

Γ also rests in local equilibrium with σ, so that:

$$\sigma(time) = \sigma[c_s(t)]$$

Balance of fluxes:

$$\frac{dc_s}{dt} = -\chi(p_s - p_0) = -\chi K_H\, c_s = -\alpha c_s$$

Solution:

$$c_s = c_{s,0}\, e^{-\alpha t}$$

$$d\sigma = -\Gamma k_B T\, d\ln c_s$$

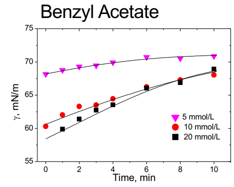
$$\sigma(t) = \sigma(t=0) - k_B T \int_{c_{s,0}}^{c_s(t)} \Gamma(c) \frac{dc}{c}$$

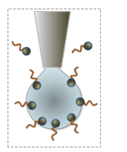
Verification of the model:

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

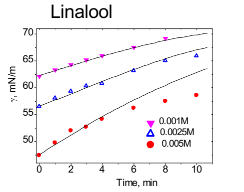
- In contrast to conventional surfactants, volatile amphiphiles evaporate from air-water interface, so that the static surface tension increases with the surface age time on a time scale of seconds.

Benzyl Acetate





Linalool



C, mM	τ_{ev}, s $(1/\alpha_{mt})$	α_{mt}, s^{-1}
5 mM	462 s	0.002165
10 mM	420 s	0.002381
20 mM	355 s	0.002817

- Continuous water flux due to evaporation accelerates the desorption of benzyl acetate molecules.
- Evaporation of linalool does not depend on the surface/bulk concentration, except a deceleration for the most concentrated solutions, in agreement with [3].

Conclusions

➢ Specific features of the interfacial adsorption and desorption behavior of volatile aroma substances – linalool and benzyl acetate – are assessed in comparison to the behavior of conventional surfactant SDS under equilibrium and non-equilibrium conditions.

➢ Specific emphasis in the discussion is put on the comparison of the surface tension data derived at different conditions / with different measuring methods including assessment of the fast-adsorbing regimes.

➢ The insights into the evaporation mechanisms have been attained by applying a simplified phenomenological theory based on the balance of fluxes.

➢ Revealed synergetic action of mixtures of conventional and volatile surfactants suggests promising applications of aroma molecules as co-surfactants in surface-emerging technologies.

References

[1] Soboleva, O. A.; Protsenko, P. V.; Korolev, V. V.; Viktorova, J.; Yakushenko, A.; Kudla, R.; Gutmann, J. S.; Tsarkova, L. A., Aroma Molecules as Dynamic Volatile Surfactants: Functionality beyond the Scent. *ACS Appl. Mater. Interfaces* **2019**, 11, 40988-40995.

[2] Soboleva, O. A.; Tsarkova, L. A., Surface Properties of Aqueous Solutions of Mixtures of Sodium Dodecyl Sulphate and Linalool under Equilibrium and Dynamic Conditions. *Colloid J.* **2020**, 82, 437-447.

[3] Danov, K. D.; Gurkov, T. D.; Stanimirova, R. D.; Uzunova, R. I., Kinetics of transfer of volatile amphiphiles (fragrances) from vapors to aqueous drops and vice versa: Interplay of diffusion and barrier mechanisms. *Colloids and Surfaces A*: **2021**, 126931.

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Conference Topics

1. Micro and Nanostructured Materials and Nanoparticles
2. Emulsions, Microemulsions, Foams and Paints
3. Surfactants, Lipids, Proteins, Peptides and Self-Assembly
4. Colloids and Interfaces related to COVID-19
5. Colloids for Delivery of Bioactives, Pharmaceutical applications
6. Colloids and Interface Science in Cultural Heritage
7. Theory, Modeling and Simulation of Colloidal Systems and Complex Fluids
8. Dynamics, Stability and Phase Behavior of Colloids and Complex fluids
9. Polymers, Polyelectrolytes, Gels, Liquid Crystals, Anisotropic Fluids
10. Liquid Interfaces and Membranes: Structure, Surface forces, Dynamics
11. Colloids in Food Science and Technology
12. Colloids and Interface Science in Energy Technology
13. Colloids and Interface Science in Environment
14. Wetting, Superhydrophobicity, Superoleophobic Surfaces and Capillarity

POSTER SESSION A

EP 3.37		**Self-Aggregation of Sugar Surfactants in Deep Eutectic Solvents and Their Solubilization of Terpenoids**	Omasta Tomas
EP 3.38	*ONLY WEB*	**Cleaning Ability of Mixed Solutions of Sulfonated Fatty Acid Methyl Esters**	Marinova Krastanka
EP 3.39		**Volatile aroma surfactants: characterization of the interfacial behaviour at dynamic and equilibrium conditions**	Theodor Gurkov
EP 3.40	*ONLY WEB*	**All-nanoparticle Layer-by-Layer Capsules – Mechanically Strong, Easily Breakable, and Good Sensors**	Li Jie
EP 3.41	*ONLY WEB*	**Controlling Reservoir Formation at the Air/Water Interface**	Carrascosa Javier
EP 3.42	*ONLY WEB*	**Effect of hybrid lipid on line tension and domain morphology of lipid vesicle**	Takkiue Takanori
EP 3.43	*ONLY WEB*	**Mucoadhesive Properties of Amphiphilic Calix[4]resorcinols Bearing Viologen or Acetate Substituents at the Upper Rim**	Kashapova Nadezda
EP 3.45	*ONLY WEB*	**Insights into the Supramolecular Self-Assembly of Porphyrin and Metallosurfactant**	Kashapov Ruslan
EP 3.46		**Thermodynamics of Malonamide Aggregation Deduced from Molecular Dynamics Simulations**	Vatin Marin
EP 3.47	*ONLY WEB*	**Interfacial Properties and Surface Aggregates of Redox-Active Surfactant**	Gokce Dick Kalaycioglu
EP 3.49	*ONLY WEB*	**Superparamagnetic colloids in rotating field: transition state from chains to disks.**	Mignolet Florence
EP 3.50	*ONLY WEB*	**Protein on Steel**	Schuurman Hent
EP 3.51	*ONLY WEB*	**Embedment of Quantum Dots in a Dipeptide Hydrogel Using Microfluidics**	Li Yue
EP 3.52		**Specific interactions of nano-ions with proteins.**	Chazapi Ioanna
EP 3.53		**Aggregation of arabinogalactan-proteins from Acacia seyal gum in low-hydration state**	Antoine-Michard Amandine
EP 3.55		**Countering the nanoparticle protein corona via binding of HSA with an Albumin-binding Hydrophobin chimera.**	Matis Ilias
EP 3.56	*ONLY WEB*	**Unravelling the adsorption mechanisms of fatty acids on calcium minerals surfaces**	Foucaud Yann
EP 3.57		**Lipo-oligoureas as a new class of antimicrobial compounds**	Burdach Kinga
EP 3.58	*ONLY WEB*	**Initial Stage of Adsorption of Monomer of SARS-CoV-2 Spike Protein on Graphene**	Benková Zuzana
EP 3.59		**Adsorption of Lutrol (Pluronic F-127) on Kappa-casein Fibrils**	Portnaya Irina
EP 3.60		**Using novel ionic liquids based on imidazolium derivatives to improve lubricating oil efficiency**	Deyab Mohamed
EP 3.61		**Detection of ovalbumin amyloid-like fibrils at the oil-water interface in oil-in-water emulsions by spinning disk confocal microscopy**	Huyst Arne
EP 3.62		**Characteristics of beta - lactoglobulin from whey protein isolate**	Gołębiowski Adrian
EP 3.65		**The effect of bubble approach velocity and surfactants on coalescence of bubbles**	Sandra Orvalho
EP 3.66		**Bubble–vortex-ring interactions: effect of surfactants on the bubble breakup**	Maria Zednikova
EP 3.67		**Metal-biosurfactant ligand complex could promote the solubilization of copper oxychloride in water**	Moldes A.B