Experimental report

18/09/2016

Proposal:	**9-10-1439**	**Council:**	4/2015

Title: Hydrophobicity inversion of short chained alcohols in microemulsions due to the polarity difference of polar and non-polar phase

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Tim SCHREINER**

Experimental team:
Tim SCHREINER
Helge KLEMMER
Lena GRASSBERGER
Carola HARBAUER

Local contacts: Isabelle GRILLO

Samples: D2O/alcohol/ethylbenzene/ethylcyclohexane/C10E7

Instrument	Requested days	Allocated days	From	To
D33	3	2	16/09/2015	18/09/2015

Abstract:

Microemulsions play an important role in many applications e.g. cleaning processes, drug transport or as reaction medium for chemical reactions. To control the nanostructure of these ternary or higher order systems temperature as well as titrating agents (e.g. alcohols) can be used. In common non-ionic microemulsions including n alkanes these alcohols act as co-solvent if they are short chained (i<3) or co-surfactant if they are long chained (i>4) thereby inducing phase inversion. While non-ionic surfactants of the general structure CiEj exhibit the same phase behaviour independent of the chemical nature of the oil used, we recently observed that this is not true for interfacially active alcohols: Methanol should act as a co-solvent in the ternary system water-ethylbenzene-heptaethyleneglycoldecylether (C10E7) solely looking at its molecular structure. However, it influences the phase behaviour as e.g. n-butanol would. Exchanging ethylbenzene by the non-aromatic, but structurally similar, ethylcyclohexane the expected effect of a co-solvent occurs. Hence, it seems very likely that the interfacial properties of alcohols also depend on the polarity difference between the two phases.

Hydrophobicity inversion of short chained alcohols in microemulsions due to the polarity difference of polar and non-polar phase

− Report on Experiment No: 9-10-1439 –

Abstract: Amphiphilic films, like in microemulsions, play an important role in many applications *e.g.* cleaning processes, drug transport or as reaction medium for chemical reactions [1]. To control the nanostructure of these ternary or higher order systems temperature as well as titrating agents (*e.g.* alcohols) can be used. In common non-ionic microemulsions including *n*-alkanes these alcohols act as co-solvent if they are short chained ($i \leq 3$) or co-surfactant if they are long chained ($i \geq 4$) thereby inducing phase inversion [2, 3]. While non-ionic surfactants of the general structure C_iE_j exhibit the same phase behaviour independent of the chemical nature of the oil used, we recently observed that this is not true for interfacially active alcohols: Methanol should act as a co-solvent in the ternary system water – ethylbenzene – heptaethyleneglycoldecylether ($C_{10}E_7$) solely looking at its molecular structure. However, it influences the phase behaviour as e.g. *n*-butanol would. Exchanging ethylbenzene by the non-aromatic, but structurally similar, ethylcyclohexane the expected effect of a co-solvent occurs. Also in the modified ternary system water – ethylbenzene – pentaethyleneglycoldecylether ($C_{10}E_5$) the same effect could be observed. Hence, it seems very likely that the interfacial properties of alcohols not only depend on the nature of the alcohol but also on the polarity difference between polar and non-polar phase. To elucidate this dependence we performed systematic scattering measurements in which the polarity difference of the phase as well as the nature of alcohol were varied to extract the interfacial composition as well as the scattering length density profile of the data to determine the very nature of the observed correlation.

SANS measurements: We performed SANS measurements in the bicontinuous microemulsion system D_2O/alcohol – ethylbenzene – $C_{10}E_7$ respectively D_2O/alcohol – ethylcyclohexane – $C_{10}E_5$ at a constant D_2O to oil and D_2O volume fraction $\phi = 0.50$ and a constant surfactant to the overall mass weight fraction γ close to the phase inversion temperature by varying the alcohol to alcohol and D_2O weight fraction ψ. Also investigations close to the efficiency points $\widetilde{X}$ of the systems were performed. For this, we used the instrument D33 with a wavelength of $\lambda = 6$ Å and with a sample-to-detector distance $d = 12.8$ m, 7 m and 2 m giving us a access to a q-range of $0.003 < q/\text{Å}^{-1} < 0.03$.

SANS results: All produced data could be described using the *Teubner-Strey* model [4] and further direct quantification of the total internal interface *S*/*V* was possible using the invariant according to *Porod* [5]. The data indicate in the system D_2O/alcohol – ethylbenzene – $C_{10}E_7$ as well as D_2O/alcohol – ethylcyclohexane – $C_{10}E_5$ close to the $\widetilde{X}$-point for all alcohols a general decrease of the domain size ξ by increasing amounts of alcohol.

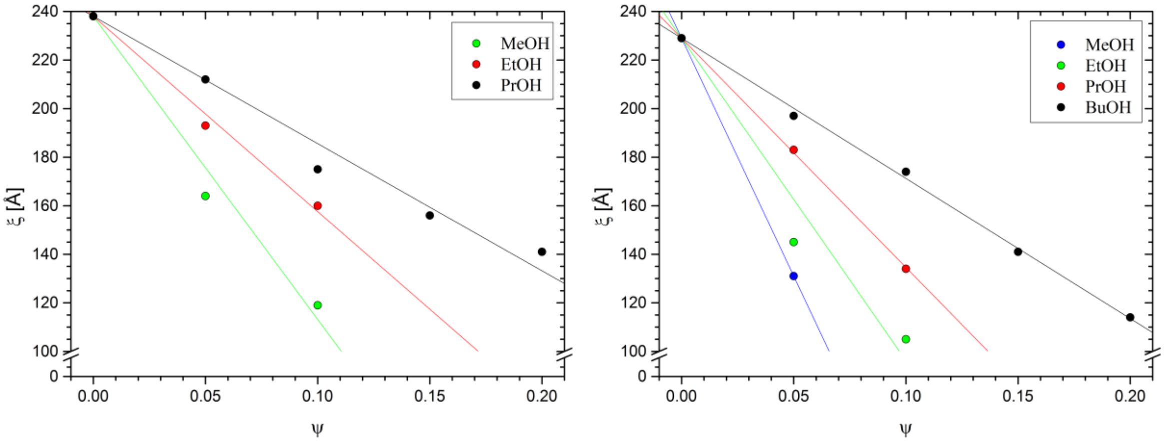

Figure 1: Correlation between the domain size ξ and the alcohol to alcohol and D_2O weight fraction ψ for the system *left:* D_2O/alcohol – ethylbenzene – $C_{10}E_7$ and *right:* D_2O/alcohol – ethylcyclohexane – $C_{10}E_5$ at a constant D_2O to oil and D_2O volume fraction $\phi = 0.50$, with methanol (black), ethanol (red), 1-propanol (green) and 1-butanol (blue).

For the system containing ethylbenzene (figure 1 *left*) the degree of domain size decrease is smaller than for ethylcyclohexane (figure 1 *right*) caused by the partial solution of alcohol molecules in the non-polar ethylbenzene phase.

Table 1: Slopes and corresponding errors for the correlation between the domain size ξ and the alcohol to alcohol and D_2O weight fraction ψ for the systems D_2O/alcohol – ethylbenzene – $C_{10}E_7$ and D_2O/alcohol – ethylcyclohexane – $C_{10}E_5$ at a constant D_2O to oil and D_2O volume fraction $\phi = 0.50$.

	ethylbenzene		**ethylcyclohexane**	
alcohol	***m* [Å]**	**Δ*m* [Å]**	***m* [Å]**	**Δ*m* [Å]**
methanol	-524	25	-577	8
ethanol	-804	34	-944	8
1-propanol	-1248	82	-1328	124
1-butanol	-	-	-1960	0

At a constant surfactant to the overall mass weight fraction γ the surface-per-volume fraction *S*/*V* in the system D_2O/methanol – ethylbenzene – $C_{10}E_7$ is unchanged with increasing methanol content whereas for D_2O/methanol – ethylcyclohexane – $C_{10}E_5$ *S*/*V* is decreased.

Table 2: Surface-per-volume fraction *S*/*V*, domain size ξ and periodicity d_{TS} of the systems D_2O/alcohol – ethylbenzene – $C_{10}E_7$ and D_2O/alcohol – ethylcyclohexane – $C_{10}E_5$ at a constant D_2O to oil and D_2O volume fraction $\phi = 0.50$ and a constant surfactant to the overall mass weight fraction γ.

ψ	**ethylbenzene**						**ethylcyclohexane**					
	methanol $\gamma = 0.135$			**ethanol** $\gamma = 0.135$			**methanol** $\gamma = 0.120$			**ethanol** $\gamma = 0.110$		
	S/V [Å^{-1}]	**ξ [Å]**	**d_{TS} [Å]**	**S/V [Å^{-1}]**	**ξ [Å]**	**d_{TS} [Å]**	**S/V [Å^{-1}]**	**ξ [Å]**	**d_{TS} [Å]**	**S/V [Å^{-1}]**	**ξ [Å]**	**d_{TS} [Å]**
0.00	0.01054	217	496	0.01054	217	496	0.01321	352	185	0.01272	201	393
0.05	0.01054	199	490	0.01054	187	496	0.01274	355	183	0.01241	183	395
0.10	0.01054	175	480	0.01054	160	507	0.01203	364	174	-	-	-

With increasing alcohol content the system shifts more and more to its $\widetilde{X}$-point where *S*/*V* reaches a minimum according to the system with ethylcyclohexane. In case of ethylbenzene *S*/*V* remains unchanged which validates that methanol acts as a co-surfactant due to that more internal interface needs to be generated and therefore the nature of an alcohol depends on the polarity difference between the polar and non-polar phase. The same effect could be observed by exchanging methanol with ethanol. Additionally, the domain size ξ in the systems with ethylbenzene is getting smaller with increasing alcohol content, whereas in the systems with ethylcyclohexane ξ increases, which correlates with the evolution of *S*/*V*.

Also contrast experiments in the microemulsion system H_2O/methanol-d_4 – ethylbenzene – $C_{10}E_7$ were performed, but the fit-model is still unclear. While all compounds except the alcohol are matched, a clear scattering pattern can be seen. This almost droplike pattern clearly proves that the alcohol aggregates and is part of the interface.

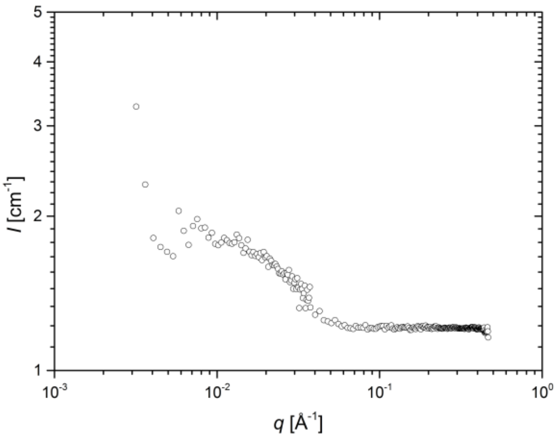

Figure 2: Scattering curve of the system H_2O/methanol-d_4 – ethylbenzene – $C_{10}E_7$.

Literature: [1] M. Kahlweit, R. Strey, *Angew Chem Int Ed Engl*, 1985, 24, 654-668.
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[3] R. Strey, M. Jonströmer, *J Phys Chem*, 1992, 96, 4537-4542.
[4] M. Teuber, R. Strey, *J Phys Chem*, 1987, 87, 3195-3200.
[5] G. Porod, in: *Small Angle X-Ray Scattering;* O. Glatter; O. Kratky, 1982.